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PROCEEDINGS OF THE SOCIETY OF ARTS.

THIRTY-THIRD YEAR, 1894-95.

THURSDAY, October 11, 1894.

THE 461st meeting of the SOCIETY OF ARTS was held at the Institute, in the Walker Building, this day at 8 P.M., President Walker in the chair.

The records of the previous meeting were read and approved. Messrs. Fred L. Bardwell, Robert P. Bigelow, Peter S. Burns, H. H. Carter, R. B. Collins, James M. Crafts, H. M. Goodwin, Simeon C. Keith, Jr., James J. Killilea, S. R. Koehler, Frank A. Laws, Richard W. Lodge, Arthur A. Noyes, William R. Roney, Harry M. Tyler, Willis R. Whitney, Henry J. Williams, Henry B. Wood, all of Boston; John Alden, of Lawrence, William W. Crosby, of Woburn, and Frank E. Sanborn, of Tufts College, were duly elected Associate Members of the Society.

The following papers were read by title:

"Proposed Formula for White Pine Posts," by James H. Stanwood.

"Cryoscopic Experiments with the Aluminates and Borates of the Alkali Metals," by A. A. Noyes and W. R. Whitney.

"Results of Tests Made in the Engineering Laboratories. I. Applied Mechanics."

"Some Experiences in Engineering Practice," by Hon. George Duncan.

"Apparatus for Measurement of Difference in Phase Between Alternating Currents," by Louis Derr.

The President then introduced Mr. Frederick E. Ives, of Philadelphia, who gave a demonstration of "Composite Heliochromy," including triple lantern projection, the photochromoscope, and permanent color printing. The paper was very fully illustrated with the lantern, and is printed in the present number of the *Quarterly*. The thanks of the Society were tendered to Mr. Ives for his very novel and interesting paper. The meeting then adjourned, and the members and their guests were given an opportunity to inspect and test the photochromoscope.

THURSDAY, October 25, 1894.

The 462d meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Professor W. T. Sedgwick in the chair.

The records of the previous meeting were read and approved. Messrs. Horace Dodd, William C. French, George W. Hamblett, J. Prince Loud, Samuel P. Mandell, and Franklin W. Pitcher, all of Boston, were duly elected Associate Members of the Society.

The following papers were read by title:

"Electrolytic Reduction of Paranitrobenzoic Acid in Sulphuric Acid Solution," by A. A. Noyes and A. A. Clement.

"Studies on the Voltaic Cell," by H. M. Goodwin.

"Close Sizing Before Jigging," by Robert H. Richards.

The Chairman then introduced Mr. George C. Whipple, Biologist in Charge, Laboratory of the Boston Water Works, who read a paper on "Some Observations on the Growth of Diatoms in Surface Waters." The paper was illustrated with the lantern, and was printed in the October number of the *Quarterly*. At its close Mr. Desmond FitzGerald and Dr. T. M. Drown spoke briefly of the practical value of a biological laboratory in the management of a city's water works,

and especially in commendation of Mr. Whipple's work for Boston. A general discussion followed, closed by the Chairman, and the meeting adjourned.

THURSDAY, November 8, 1894.

The 463d meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., President Walker in the chair.

The records of the previous meeting were read and approved. Messrs. William S. Hadaway and Frank H. Thorp, of Boston, Archibald T. Martin and Walter L. Martin, of Chelsea, Edward S. Morse, of Salem, Albert Ball Tenney, of Everett, George K. Thompson, of Malden, Charles R. Walker, of Cambridge, and George C. Whipple, of Newton Centre, were duly elected Associate Members of the Society.

Mr. Blodgett, for the Executive Committee, proposed an amendment to the By-Laws, making the quorum of the Executive Committee three instead of four, as at present. Under the rules it was laid over until the next meeting.

The President then introduced Mr. William Danmar, of Brooklyn, who read a paper on "The Colonial Style of Architecture." The paper was very fully illustrated with the lantern, and is printed in the present number of the *Quarterly*. The President extended the thanks of the Society to Mr. Danmar, and declared the meeting adjourned.

THURSDAY, November 22, 1894.

The 464th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Dr. T. M. Drown in the chair.

The records of the previous meeting were read and approved.

The following papers were read by title:

"Results of Tests in the Engineering Laboratories. II. Steam and Hydraulic Tests."

"The Summer School of Mines," by Robert H. Richards.

Action on the proposed amendment to the By-Laws was postponed until it should have been approved by the Committee of the Corporation.

The Chairman then introduced Mr. Arthur D. Little, of Boston, who gave an address on "Paper-Making and the New Uses of Wood Fibre," and showed a large collection of specimens illustrating it. The Chairman extended the thanks of the Society to Mr. Little, and declared the meeting adjourned.

THURSDAY, December 13, 1894.

The 465th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Mr. George W. Blodgett in the chair.

The records of the previous meeting were read and approved. Messrs. Amos Binney, of Boston, Charles F. Warner, of Cambridge, and Leonard C. Wason, of Brookline, were duly elected Associate Members of the Society.

Mr. I. H. Farnham, of the New England Telephone and Telegraph Co., read a paper on "Electrolysis of Pipes — the Cause and Prevention." The paper was fully illustrated with the lantern. The meeting then adjourned.

CLEMENT W. ANDREWS, *Secretary.*

COMPOSITE HELIOCHROMY.

By F. E. IVES.

Read October 11, 1894.

Composite Heliochromy is a system of photography which is capable of automatically and accurately reproducing the colors of any objects that may be photographed, although the direct action of light upon the sensitive plate does not produce colors, but only a record of colors, which record is afterwards translated into color again to the eye by either of two distinct methods. Three negatives are required to produce the color record, because there are three colors that can be made to reproduce all others by mixture in suitable proportions.[1] It is the function of the negatives to secure a correct mixture of these three colors in the composite color photograph.

The three colors which will mix to reproduce all others are the spectrum red below Fraunhofer line C, the spectrum green at E, and the violet above G. Equal parts of the green and red produce a very perfect yellow, and mixtures in other proportions produce all shades of yellow-green and orange. Equal parts of the violet and red produce a bright pink, and equal parts of the green and violet produce a bright cyan-blue. A mixture of the three in correct proportions produces a perfect white.

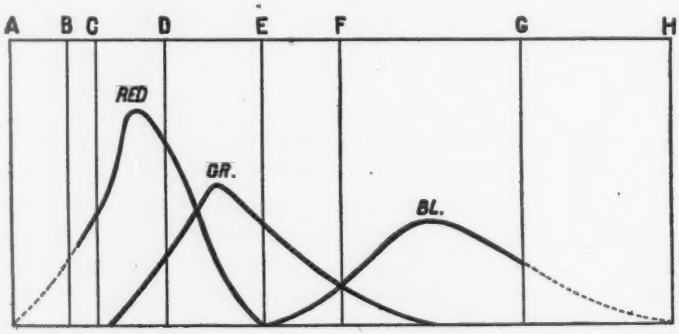
The colors produced by such admixtures are not, however, physically identical with the spectrum colors which they represent to the eye, and appear to be so only to people having normal color vision and under normal conditions. For instance, even to a person of normal color vision the mixture of red and green may be made to appear either red or green by interposing suitable color screens which do not alter the hue of the spectrum yellow in the least.

This method could not, therefore, be said to actually reproduce all natural colors if colors were objective, as taught by Newton and

[1] A partial exception is the spectrum blue-green, which is slightly degraded by admixture of white in the reproduction.

Brewster. But color is merely a sensation, like the feeling of heat, cold, etc., and therefore to produce the same effect upon the nerves of vision is to produce the same sensation, which is the same color.

The explanation of all this is, briefly, that there are three fundamental color sensations, which, it is convenient to assume, are due to three kinds of nerves in the eye (although some other explanation may eventually be found), and most of the spectrum rays excite two fundamental sensations at once, in different degrees. Maxwell believed that the red rays below C, the green at E, and the violet near G, the only colors which can be made to reproduce all others, excited exclusively the respective fundamental color sensations. By means of a very ingenious optical device, which is known as Maxwell's color box, he reproduced all of the other spectrum colors to the eye by mixtures of these, and plotted curves showing exactly what mixture was necessary to reproduce the color of any point in the spectrum.



Recent investigations have established the fact that the green of the spectrum does not accurately represent the fundamental green sensation, but that sensation degraded by considerable admixture of red and a little violet. But there is no other means of exciting the green sensation so exclusively in a person having normal color vision as by exposing the retina to these particular spectrum rays, and a successful system of composite heliochromy must therefore be based upon such measurements as were made by Maxwell. Abney has obtained somewhat more accurate results, but the differences are of very little practical importance in this connection, because they are due chiefly to the use of purer colors with which to make the mixtures, and Max-

well's "fundamentals" are as near correct as anything which it is practicable to use for reproduction purposes in composite heliochromy.

The application of Maxwell's color curves to composite heliochromy is most readily shown by assuming that we wish to reproduce the spectrum itself. We know that in order to do so we must mix the three colors which Maxwell assumed to be the fundamentals, and that for each part of the spectrum we must mix them in the proportion indicated by the height of the color curves in the diagram. One negative represents the red, and all of the spectrum rays from A to E must act in producing it in such proportion that it will show a distribution of density corresponding to the first curve of the diagram. We may secure this by exposing through a suitable orange-colored screen a rapid gelatine-bromide plate sensitized by cyanine, or the same result can be obtained with commercial "isochromatic" plates by exposing through a compound color screen of brilliant yellow and fuchsine. Another negative which represents the green must show a density curve corresponding to the second curve in the diagram, and another, representing the blue-violet, a density curve corresponding to the third curve in the diagram. These negatives can also be made on "isochromatic" plates by exposing through suitable color screens. These three negatives constitute, by their distribution of light and shade, a record of all the colors of the spectrum, and represent the first stage of the process of composite heliochromy, which is the same for all objects, because a procedure that will secure a correct reproduction of each and every separate spectrum color must reproduce all mixed colors as well.

Our color record in no way suggests color, but if we make lantern slides from it and project one with red light, one with green, and one with blue-violet in proper register upon the screen, the mixture of the three colors, regulated by the variations of density in the positives, will produce a perfect reproduction of the spectrum we photographed.

The process as described seems complicated and roundabout, but the production of the color record has been so simplified by the invention of a special camera that it is exactly as easy as the production of an ordinary photographic negative, the three images being made by simultaneous exposure on a single plate. It was necessary to simplify the operation of the process in this way in order to make it available to unskilled operators, or even to make it reliable in the hands of the most skillful. It was also desirable to provide a means of translating

the color record into color more simple and convenient than by lantern projection, and this is accomplished in the photochromoscope, a table instrument not much larger than a stereoscope. In this instrument each of the monochrome images of the chromogram is seen through its appropriate color screen, but the three are blended into one on the retina, reproducing the colors so perfectly that one appears to see the object itself instead of a picture.

The photochromoscope and photochromoscope camera and process constitute a method of reproducing the natural colors which is as simple in operation as stereoscopic photography. And the instrument can, of course, be made stereoscopic, so as to combine stereoscopic relief with color. Nachet, of Paris, claims to have done this in a new instrument of his own design, in which one eye sees the red and green images (blended into one) and the other eye the blue-violet; but this instrument is really very defective, both as a stereoscope and as a photochromoscope. It is defective as a stereoscope, because the images seen by the two eyes are different in color, which tires the eyes; and the stereoscopic effect is also imperfect for strongly colored objects, which are sometimes scarcely visible in one image, while strongly defined in the other. It is defective as a photochromoscope, because colors cannot be perfectly blended except upon the same retina, the impression being a changeable one, as the attention is involuntarily and unconsciously shifted from the sensation in one eye to that in the other in rapid succession. This curious effect may be seen by placing a deep ruby-red glass in front of one eye and a deep green in front of the other, and looking at a white object; with yellow and blue glasses the effect is of the same character, only less marked and irritating. In my own stereochromoscope each eye sees an image complete in color and detail, and it is only necessary to cover some of the positives, so as to practically convert it into a Nachet instrument, in order to make the result intolerable by comparison.

By an extension and further complication of the system permanent color prints can be made, either as transparencies on glass, suitable for lantern slides, or prints upon paper; but absolutely satisfactory results can be obtained only in the photochromoscope, and in my opinion all other applications of the system are of less importance, because they are more complicated, more difficult, and less perfect in proportion to their complication.

The production of permanent color-print lantern slides, however,

promises to become sometime in the future an important industry. Already it has reached such a stage of perfection in my own hands that although it costs far more to make these pictures than ordinary hand-painted ones, the results are so exquisite that I doubt if anybody would use painted slides who could get these at ten times the cost; and I think their first use as popular lecture illustrations this year will mark the commencement of a new era in lantern lecture work.

These lantern slides are made from the photochromoscope negatives by a comparatively simple process, which is not difficult to carry out, except that it requires a master of the science of the subject to recognize and keep to the conditions which guarantee a high degree of accuracy in the results. A thin sheet of clear celluloid coated with bichromatized gelatine is exposed to light under the negative, the light passing through the celluloid to the sensitized gelatine. The resulting print, which shows the three images of a chromogram in a delicate brown color, is placed in hot water, which dissolves away all of the gelatine that is not rendered insoluble by the action of light and leaves the images in very low relief in transparent gelatine, the shadows of the pictures being represented by various thicknesses of the gelatine and the extreme high lights by clear celluloid. The three images are then cut apart with scissors and each colored up by soaking in a solution of a dye the color of which is nearly complementary to the fundamental sensation which that image represents. The dye does not color the celluloid, which merely serves as a support for the gelatine picture, but is taken up by the gelatine in proportion to its thickness. Relatively too much or too little color in any one print will destroy the accuracy of the coloring in the composite whole, and in practice it is almost always necessary more than once to wash out the color and immerse in the dye again for a longer or a shorter time. The colored prints are superposed so as to bring the three images into register and make them appear as one, and if the deepest shadows are then a neutral black the colors should be right throughout all the shades of the picture, and will be, if the correct printing colors are used and the known theoretical conditions of success adhered to. When satisfactory, they are cemented up between glasses with Canada balsam and fastened by a paper binding on the edge.

In triple lantern projection and in the photochromoscope the image of the red sensation is projected with red light, the green with green light, and the blue-violet with blue-violet light. In three-color

printing the image of the red sensation is a cyan-blue print, the green a pink print, and the blue-violet a yellow print. This is confusing to most people, but it is easy to show that it comes to the same thing. When we have made a white disk on the screen by means of the triple lantern and its red, green, and blue-violet lights, we shall find that if we insert a positive in the red section the result upon the screen is a cyan-blue picture on a white ground, looking exactly like the cyan-blue print we have to make from the negative of the red sensation in three-color printing. The same for the other images, which are pink and yellow. We get no black shadows on the screen until there is a positive in each section. In the same way we get no blacks in three-color printing until all three prints are put together.

The function of the uncolored positive in triple projection and the colored positive in triple printing is, therefore, the same, *i.e.*, to suppress by its shadows those rays which excite powerfully the fundamental sensation which that positive represents. In triple printing the positive of the red sensation is a cyan-blue, which absorbs first of all the red and orange rays, but also, progressively, the yellow and green-yellow, freely transmitting only those which excite most exclusively the other two sensations. The positive of the green sensation is a pink, which absorbs first of all the green rays, but also, progressively, the yellow and green-blue. The positive of the blue-violet sensation is a yellow, which absorbs first of all the violet rays, but, progressively, the blue and blue-green. These colors are called the printing colors, and are the only ones that are capable of reproducing all others by absorption, as red, green, and blue-violet light will by mixing.

It will be observed that the printing colors are not "red, yellow, and blue," but pink, yellow, and green-blue. The fundamentals are obtained by superposing films of these colors two and two. Thus, it requires a combination of the pink and yellow to produce red, the pink and cyan-blue to produce true violet-blue, and the cyan-blue and yellow to produce green. Each printing color represents the abstraction from white light of one of its fundamental color elements, and Captain Abney has therefore suggested that the fundamentals be termed + R, + G, + V, and the printing colors — R, — G, — V. The fundamental violet is the spectrum color, and not the violet of commerce, which is a purple.

By a still further extension of the system prints are made on

paper by machine printing, with half-tone process blocks. We have heard a great deal of this method for two years past, but it is not, in my opinion, capable of competing with chromolithography for commercial purposes at the present time. The photochromoscope system is the only one that can be made practically available by amateur photographers, and the results are almost ideally perfect. The lantern slide process is far more difficult to carry out in a perfect manner, and the results, although beautiful, are certainly not quite so perfect. The machine printing process is still more difficult to carry out in a really satisfactory manner — so much so as to make it at present commercially impracticable — and the results are at best very inferior.

THE COLONIAL STYLE OF ARCHITECTURE.

By WILLIAM DANMAR.

Read November 8, 1894.

The main cause of the failure of development of a modern American style of architecture is the fact that, in consequence of the so much extended means of communication and publication, we know now the styles of every country and every period, and are so overwhelmed by this immense amount of varying architectural productions that we cannot as yet concentrate our efforts in one particular line and work in one particular style.

The history of architecture shows that a style was the natural outgrowth of the concentrated evolution of the entire architecture of a nation or a period. During the eighteenth century the conditions in America were favorable for the development of a distinct style, because this country was isolated and the knowledge of architecture limited to one style, that of the later Renaissance; and such limitation will always result in the development of a new style. In this country it resulted in the colonial style of architecture, which is really the only one that can be termed distinctly American. Since this style has in late years been revived and become the leading one for country residences, the study of it is interesting, both from the historical and professional standpoints.

The architectural profession uses the term of "Colonial Architecture" to indicate the architecture in America from the beginning of colonial times to the introduction of Greek architecture at the beginning of the present century; consequently some forty years of the existence of the republic are included, which shows that the change of government did not produce a change of the style of architecture.

The colonial style is identical with the style of the American Renaissance, or the American branch of the great new birth of Roman art, and especially of the later Renaissance of the eighteenth century, which in every country of the civilized world was altered and

adjusted to the various conditions to such an extent as to produce a number of national Renaissance styles. Our colonial style is one of them; it is, therefore, just as much a national style as, for instance, the English or the German or the French style of the Renaissance of the eighteenth century.

There are three periods of colonial architecture: first, the colonial period of the seventeenth century; second, the provincial period, from the beginning of the eighteenth century to the time of the Revolution; and third, the federal period, from the birth of the nation to about the year 1815, when the stout Greek porticoes made their appearance. Colonial architecture is also subdivided into three branches: the English colonial of New England, the Dutch colonial of New York and vicinity, and the French colonial of the South. The colonial architecture of New England is considered the best and most elaborate, and has therefore been made the basis of the modern revival of the style which began in Boston and has now spread all over the country.

The architecture of the colonial period was necessarily crude and plain, owing to the limited facilities for artistic work. The Fairbanks house in Dedham, Massachusetts, built in the year 1636, is one of the oldest, if not the oldest, frame dwelling house in New England. There are also a number of frame cottages in Concord, Massachusetts, of the seventeenth century, of which the Minot house is one of better design than most of them. All these buildings, however, which are now ruins, do not yet show a style of their own, but are simply imitations in wood of the stone architecture of Europe; yet this very imitation was the main cause of the gradual development of the colonial style, for there is nothing influencing architecture so much as the material of which it is made.

There is one building of the colonial period of the seventeenth century on which one of the principal features of the colonial style originated; it is the Unitarian Church at Hingham, Massachusetts, built in the year 1681. It still exists, and is now the oldest church in America; it is not a ruin, but in good condition, because the exterior woodwork has been renewed twice and the best care has been taken of it. But it is only by careful repairs that this sole relic of the Puritan wooden meeting houses of the seventeenth century has been preserved so long; all the others have rotted away. The architects of the meeting house at Hingham were old sea captains, who prepared

for themselves a gallery at the top of the large, plain, hip roof by creating a small deck roof with a slender turret in the center and a railing around it. On this roof gallery the sea captains then stood and observed the ships on the near-by water, as they did before from the ship's bridge; for this reason that old meeting house was, and is still, called "the Ship," or by this time, "the old Ship." The gallery on the roof was imitated, became a matter of fashion, and finally one of the principal features of the colonial style, which we find again on almost every important building of the eighteenth century, where in some cases it was elaborated to what is termed "the sky parlor."

The provincial period, consisting of the first three quarters of the eighteenth century, produced more elaborate buildings, on account of the growing wealth of the country and the increased facilities for obtaining implements and materials. The greatest feature of the architecture of this period was the gambrel roof, which was highest developed at about the middle of this period. The Greenough house in Jamaica Plain, built in 1730, and the Dalton house in Newburyport, built in 1750, are still existing prominent representatives of the gambrel roof architecture of the provincial period. But its most prominent representative was the Hancock mansion in Boston, which has in late years been torn down to make way for modern improvements. It was built in the year 1737 by Thomas Hancock, and after his death came into the hands of Governor John Hancock, who made it a center of colonial society. The Hancock mansion, which is shown in our illustrations, was built of brown stone and had a fine gambrel roof, with three dormer windows to the front, a railing on the deck roof, etc. Over the entrance door was a balcony, and the balcony door was adorned with a cap that terminated with the volutes of the barock style. This building has become the pattern for a large number of modern buildings of the colonial style, and has also been the model for the Massachusetts House at the Chicago Fair. Our second picture shows a modern house in Andover, Massachusetts, designed by Mr. Kelly, of Boston, in the style of the gambrel roof architecture of the first half of the provincial period. Since the Hancock mansion is the principal pattern for these buildings of the modern revival, we may term this "the Hancock House Colonial Style."

After the year 1740 the hip roof with roof gallery took the place of the gambrel roof, especially on brick buildings, because it saved the brickwork of the gables. The Pettingrew house in Ports-

FIG. 1. HANCOCK HOUSE, BOSTON.

FIG. 2. MODERN COTTAGE, ANDOVER (J. T. KELLEY).

FIG. 3. LONGFELLOW HOUSE, CAMBRIDGE.

FIG. 4. MODERN COTTAGE, BROOKLINE (RAND AND TAYLOR).

mouth, New Hampshire, and the Emerton house in Salem, Massachusetts, are fine specimens of those plain, square, hipped-roofed brick houses of the middle of the eighteenth century, which have found but little imitation in modern times. But that feature of colonial architecture which more than any other entitles it to a style of its own had by this time been well developed, and that is, the exceptionally slender proportions of details. The minute dentals, moldings, *papier-maché* ornaments, so very delicate and fine, are all consequences of the fact that the art forms or trimmings of all these buildings, even of the brick buildings, were made of wood, which not only permitted but really called for such delicacy. In this respect of details, the colonial style has deviated further from classical proportions than any other style of the Renaissance. This "delicate feeling" of colonial details has been credited to "the refinement of the colonial people," which, I think, is a decided mistake; for, not considering whether there was such a special refinement or not, which I doubt, the mere fact that these details of stone architecture were imitated in wood gives a sufficient technical explanation of their development into these slender and fine proportions, which reached their almost "unnatural" culmination on the mantles of the federal period.

In the year 1759 a man by the name of Craigie erected a fine mansion in Cambridge, Massachusetts, which is now called "the Longfellow house," because it has been the residence of the poet Longfellow. During the Revolutionary War it was the headquarters of General Washington. This building, of which we show a view, marks the beginning of the style of the federal period, and is still its main representative. The Taylor house in Dorchester, built in 1780, and a number of other grand old mansions of the federal period are largely patterned after the famous Craigie mansion or Longfellow house. Its principal features are a large hip roof with a roof gallery, and in the center a gable with a semi-round window flanked by two dormer windows. At each end of the building is a wide piazza, and the front wall is adorned with four heavy pilasters of the barock style. These principal features are very good and well proportioned, while the details are rather heavy and not as strictly colonial as those of other buildings of that period. But the general outlines of the Longfellow house have become great favorites in the modern revival of the style, even more so than the outlines of the Hancock house; therefore "the Longfellow House Colonial Style" is now the second principal branch

of that architecture. The fourth picture shows a modern cottage in Brookline, which is designed in the Longfellow house colonial style, though it varies in many details from the original.

Besides these two principal branches there are other less important branches of the style; one of them is represented by the Babson house in Newburyport, which has been the pattern for a very fine modern mansion in Braintree; this branch is similar to that of the Longfellow house, except that instead of a center gable it has a third dormer window on the front roof. Another branch of the style is patterned after the Watson house in Providence, Rhode Island, now torn down; it has an additional railing at the foot of the large hip roof, directly over the outside walls.

Among the modern cottages of the colonial style there are some which show an attempt to combine to a harmonious design all the principal features of the style of the federal period, which should really be termed "the Federal Style of architecture." A very successful and most beautiful building of this kind is the grand colonial mansion of Mr. Gordon Reed, in Cowesett, Rhode Island, designed by Gould & Angell, of Providence. A number of other similar mansions in New England are also quite complicated designs in this style; they are somewhat too complicated and too "broken up" for colonial mansions, but they show that the architecture of the federal period furnishes us enough varying details to answer for all purposes; and this will be the more so after the architects or students of architecture have brought to light all there is in that architecture (for there can be no doubt but that there is a great deal more in it than we have got out of it so far) and then have systematized it and placed it in the hands of the profession "ready for daily use." Those who should do that would do a great service to the national architecture of this country.

STUDIES ON THE VOLTAIC CELL.[1]

By H. M. GOODWIN, Ph.D.

Received October 19, 1894.

Introduction.

Of the many scientific problems which have presented themselves during the last century for solution, probably no single one has excited more universal interest or been more widely discussed than that of the origin of the electromotive force in the voltaic cell. As is well known, opinion as to the cause of the development of electrical energy in the cell has from the very first been more or less equally divided, the views of the two respective schools being set forth in the well-known *chemical* and *contact* theories. It is not proposed in the present paper to reënter upon any discussion of these repeatedly contested views. Professor Lodge's[2] admirable *résumé* and discussion of the whole subject a few years since leaves, indeed, little to be added; and with the principal conclusion of his paper, namely, that the true seat of the E. M. F. of a cell is at the metal-liquid junction, I wholly agree.

But in tracing back the principal seat of E. M. F. to the metal-liquid junction, only the first step towards establishing a satisfactory theory of the cell is made. There still remains the more fundamental question as to what energy transformation takes place when a metal and liquid are brought in contact, and of formulating a theory by which the potential difference (*P. D.*) thus produced can be calculated from other measurable physical quantities. That thermochemical data of the reactions taking place in a cell alone furnish no true measure of the E. M. F. is now well known from the investigations of Gibbs and v. Helmholtz. To what energy transformation shall we then ascribe the development of voltaic electricity?

For a satisfactory answer to this question we have in the first

[1] Translated and rewritten, with omission of experimental details of the investigation, from Zeitschrift für physikalische Chemie, 13, 577, 1894.

[2] Lodge, Philosophical Magazine, 19, 561, 1885.

instance to thank Professor Nernst,[1] who, in his paper on the *Electromotorische Wirksamkeit der Ionen*, not only developed a theory of liquid cells, which has been well confirmed by experiment, but also a theory of the development of electrical energy at the junction of a metal and liquid. This theory, which for reasons will appear directly may appropriately be called the *osmotic* theory of the cell, was further developed and followed out in its consequences by Ostwald in 1893, with the result that in all probability the following general law holds true: *The P. D. between a metal and a liquid is determined by a constant characteristic of the metal (its electrolytic solution pressure) and by the partial osmotic pressure of the kathions of the metal in the solution.*

This law may be considered as an extension of Nernst's original statement of the theory, in as much as it should hold for very small as well as greater concentrations of the kathions. As no experimental data by which this generalization of the theory could be tested was at hand, I undertook, at the suggestion of Professor Ostwald, an investigation with this point in view, the results of which are embodied in this and a following paper. It is with pleasure that I take this opportunity of expressing to Professor Ostwald my sincere thanks for the interest and numerous suggestions which he accorded me throughout my work.

Before considering the experimental part of this investigation it seems desirable to review and formulate the fundamental ideas on which the theory rests, especially as a statement of the osmotic theory has not as yet appeared in English. The development here given is in accordance with the most recent investigations, and differs, therefore, somewhat from that originally given by Nernst in 1889.

Osmotic Theory of the Voltaic Cell.

A reversible electrode may be defined as one whose surface remains chemically unchanged, or, in other words, does not become polarized by the passage of a current through it in either direction. For convenience we will divide, with Nernst, all reversible electrodes into two classes, namely:

Electrodes of the first kind, consisting of a metal in a solution of one of its salts, *e.g.*, zinc in zinc chloride, copper in copper sulphate, etc.

[1] Nernst, Zeitschrift für physikalische Chemie, **4**, 129, 1889.

Electrodes of the second kind, consisting of a metal in a solution which is *saturated* with a more or less difficultly soluble salt of the metal, and contains in addition a second soluble salt whose anion is identical with that of the first salt, *e. g.*, mercury in a zinc sulphate solution containing an excess of mercurous sulphate, one of the electrodes of the well-known Clark cell. We will call the salt with which the solution is saturated the depolarizer. Regarding its solubility we will make no assumption whatever; it may be comparatively soluble or may belong to the class of so-called insoluble salts, the one condition to be fulfilled being that it shall be present in excess, so as to insure saturation of the solution with respect to it.

Elements made up of two such reversible electrodes, be they both of the first kind, as in the Daniell element, or one of the first and one of the second kind, as in the Clark element, or, finally, both of the second kind, are themselves reversible and belong to the class of constant elements. In what follows it is to such elements alone that our considerations will apply.

If we consider any closed element of the above type it is clear that the E. M. F. is equal to the sum of the potential differences at the several heterogeneous junctions in the circuit. In general these junctions are:

1. Metal-liquid.
2. Liquid-liquid.
3. Liquid-metal.
4. Metal-metal.

As 1 and 3 are the same, there are really but three different junctions to consider. We will consider them each in turn.

Metal–Metal Junction.[1]

A satisfactory theory to account for the development of electrical energy at the junction of two different metals, it must be admitted, has not as yet been proposed. The several explanations which have been put forward by Lodge, Ostwald, and others are little more than possible hypotheses, with hardly the claim to the consideration of a theory.

[1] It need hardly be mentioned that the contact force here considered is not to be confounded with the "volta effect," *i. e.*, the *P. D.* of a metal-gas junction.

Regarding the magnitude of this *P. D.* we know much more, however. Although not directly measurable by the ordinary electrometer or galvanometer methods, its true value has been repeatedly indirectly measured by the Peltier effect and by the known relation between the thermo-electric coefficient of a metal pair and its potential. Determinations of the true contact force of metals by these methods have proved it to be very small, rarely exceeding a few milli-volts except for a few exceptional combinations, such as antimony and bismuth. It may usually be neglected, therefore, in comparison with the total E. M. F. of a cell.

Liquid–Liquid Junction.

The existence of a *P. D.* at the junction of two liquids has been known since the time of Volta, and numerous investigations have been carried out to determine its cause. Until very recently, however, no results of a general character were obtained. All attempts to explain this development of electrical energy by chemical actions taking place between the solutions proved fruitless, as it was shown by Worm Müller that very considerable potential differences existed between solutions having no chemical action whatever on each other. That the effect was dependent on the relative concentration of the solutions in contact and on their nature was, however, well established by these earlier investigations.

The first step towards the solution of this problem was made by v. Helmholtz in 1882, who showed by purely thermodynamical considerations that the E. M. F. of certain concentration elements could be calculated from the vapor pressures of their solutions and Hittorf's transference numbers. It was not until 1889, however, when Nernst, armed with the modern theory of solutions and the dissociation theory, took up the problem, that a clear conception of the phenomena taking place at the junction of two electrolytes was reached. He had already shown a year previous in a paper on the diffusion of electrolytes that a *P. D.* must be developed at the junction of two electrolytes when brought in contact with one another, its amount depending on the difference of the velocity of migration of the ions present and on the relative concentration of the solutions.

By choosing suitable electrolytes, as potassium chloride, for example, in which the velocity of migration of both anion and kathion is nearly the same, the *P. D.* at the liquid junction can be reduced

to practically zero. Under any circumstances the *P. D.* of liquid elements is small. The further development of Nernst's theory by Planck and its excellent confirmation by the investigations of Negbauer have put the theory of liquid cells on a sure and calculable basis, at least as far as binary electrolytes are concerned.[1] We shall in what follows choose our solutions such as to make this *P. D.* either negligible or so small that it can be regarded as a small correction term, and may therefore without further ado dismiss this source of E. M. F. from our considerations.

Metal–Liquid Junction.

We must from the preceding considerations seek the principal seat of the electromotive force of a cell at the metal-liquid junction. Indeed, independent of all speculation, we are driven to this conclusion at once in the case of a rather remarkable element consisting of silver electrodes immersed in normal solutions of silver nitrate and potassium cyanide, respectively, which has an electromotive force of over a volt. Here the *P. D.* at the silver-silver junction is necessarily zero, at the liquid-liquid junction a few hundredths of a volt at most, from which there remains no other alternative than ascribing the very considerable E. M. F. of the element to the potential differences between the electrodes and the solutions.

To explain now the development of electrical energy on bringing a metal in contact with a liquid, we must assume that no substance when brought into a liquid is absolutely insoluble. That such must be the case is a consequence both of the thermodynamical and of the kinetic theory of solutions. The solubility may be so small as to be quite beyond all chemical means of detection, yet nevertheless a definite solubility must be ascribed to every substance in every other under given conditions of temperature and pressure. When a substance is brought into a solvent not saturated with respect to it, solution at once takes place until the concentration of the variable phase, *i. e.*, the solution, reaches a perfectly definite amount, when solid substance and solution are in equilibrium with each other. If, on the other hand, the solution into which the substance is brought is

[1] For a complete treatment of the theory of liquid, concentration, and diffusion elements, see Ostwald, Lehrbuch, II, 1, 831 (2d edition, 1893), and the original papers of Nernst, Zeitschrift für physikalische Chemie, 4, 129, 1889; Planck, Annalen der Physik und Chemie, 39, 161, 1890; ibid., 40, 561, 1890; Negbauer, ibid., 44, 737, 1891.

supersaturated, precipitation takes place until, again, the same concentration characteristic of the equilibrium between the substance and solution is reached. Exactly analogous considerations, of course, hold for the equilibrium of liquid and vapor. In other words, we may say that when equilibrium is established between a liquid and its vapor or a solid and its saturated solution the condition energy of the one phase is held in equilibrium by the volume energy (either as gaseous volume energy or osmotic energy) of the other.

These considerations hold true whether the process of solution is a simple one, as is the case of many organic substances where the dissolved substance goes into solution as molecules, or whether it is accompanied by electrolytic dissociation, as in the case of the solution of acids, bases, and salts. In the latter case, however, there exists simultaneously with the equilibrium between solid substance and dissolved molecules a second equilibrium between these latter and their dissociation products, the ions. These two conditions are formulated in Nernst's two laws of solubility effect, which will be discussed at length later on.

As the condition of equilibrium between a substance which dissociates and its solution is more complicated than that of a simple molecular solution containing no ions, it is not astonishing that the condition of equilibrium between a metal and a liquid is still more complicated, for in this case a further peculiar condition must be fulfilled, namely, that, as far as we know, a metal can go into solution only as positively charged ions.

With this condition in mind let us consider the equilibrium between a metal and liquid a little nearer, and, in the first place, a case analogous to that of a substance brought into an unsaturated solution, *e.g.*, zinc in a solution of a zinc salt. The salt is, of course, more or less dissociated into its ions according to the concentration of the solution. Let the partial osmotic pressure of the Zn-ions be denoted by p. As soon as the zinc is brought into this solution it begins to go into solution as positively charged ions. The exactly equal quantity of negative electricity which must necessarily be simultaneously set free remains on the zinc electrode, thus charging it negatively; in other words, a *P. D.* is instantly developed between electrode and solution. The negatively charged zinc now attracts electrostatically the positively charged Zn-ions in the solution, thus forming a "double layer," first described by Helmholtz, and this attractive force, acting in the

same direction as the osmotic pressure of the zinc ions, tends to prevent further solution of zinc. By Faraday's law each gram equivalent of an ion carries with it the enormous quantity of electricity of 96,540 coulombs; hence the electrostatic attraction resulting from an exceedingly small, indeed unweighable, number of ions sent out from the zinc, very quickly becomes enormous. The equilibrium between zinc and solution will, in fact, on account of the enormous increase in the electrostatic attraction with increasing solution of metal, *i. e.*, formation of ions, be reached practically instantly, under which condition the *intensity* of the condition energy of the zinc tending to send Zn-ions into solution is exactly balanced by the sum of the osmotic and electrostatic opposing intensities in the solution. Analogous to the *solution pressure* in the case of ordinary substances, we will call this intensity in the case of metals their *electrolytic solution pressure*, and will denote it by P. Hence in the above case

$$P = p + f(s)$$

where s denotes the number of ions sent out from the electrode to establish the equilibrium. The function $f(s)$ is probably determined by the ordinary laws of electrostatics.

Let us suppose now that the number of Zn-ions in the solution becomes greater and greater, *i. e.*, that p increases. Evidently the number of ions which must be dissolved from the zinc to establish equilibrium will become less and less, *i. e.*, the term $f(s)$, and hence the *P. D.* between metal and liquid corresponding to it becomes smaller, both approaching simultaneously the value zero. This limiting case is evidently reached when $p = P$, in which case no zinc goes into solution and no *P. D.* at the junction is developed. An analogous condition is that of a body brought into an exactly saturated solution. Here the condition for equilibrium is already fulfilled. In this limiting case the equilibrium between metal and solution is held solely by an opposing osmotic pressure, or, in other words, by volume energy. Electrical energy does not enter into consideration at all. We may consequently define the electrolytic solution pressure P of a metal as equal to that opposing osmotic pressure which would reduce the *P. D.* between the metal in question and a solution to zero.

Let us consider now a case in which $p > P$, *e. g.*, a copper or mercury electrode in a solution of one of its salts. This case is analogous to that of a substance brought into a supersaturated solution.

Exactly as under such conditions solid substance is precipitated out of the solution until the osmotic pressure corresponding to the equilibrium condition is reached, so here when, *e.g.*, copper is brought into a solution of copper sulphate some of the Cu-ions present precipitate out as metallic copper. They do this by giving up their positive charge to the electrode, which thereby becomes positively charged, while the solution on account of the excess of SO_4-ions remaining in it becomes negatively charged. Thus a *P. D.* is again instantly developed between metal and solution, but in this case in the opposite direction to that in the case of zinc — a fact long known from experiment. The immediate consequence of this *P. D.* is a repulsion between the positively charged electrode and the positively charged Cu-ions, which repulsion acts *against* the osmotic pressure p in the solution. From considerations similar to those above it is evident that an exceedingly small precipitation of Cu-ions suffices to cause an electrostatic repulsion sufficient to establish equilibrium. In this case

$$P = p - f(s).$$

It follows, therefore, that if by any means the osmotic pressure p can be varied within sufficiently wide limits so that $p > P$ on the one hand, and $p < P$ on the other, the *P. D.* between metal and liquid should be reversed. This theoretical consequence of our theory is, in fact, experimentally verified in the case of certain metals as, *e.g.*, mercury. Ostwald's approximate calculation of P for this metal gives the exceedingly small value of about 10^{-15} atmospheres. Mercury must, therefore ($p > P$), be positive in any mercury solution, as, in fact, experiment shows it to be. In a solution of potassium cyanide, however, its potential becomes reversed, the electrode becoming *negatively* charged against the solution. The reason for this is clear, for in presence of potassium cyanide mercury salts form the complex salt $K_2Hg(CN)_4$, which dissociates not into Hg-ions, but into K- and complex $Hg(CN)_4$-ions. The action of the cyanide is, therefore, to withdraw the Hg-ions present from the solution, thus diminishing their osmotic pressure. This goes on, the *P. D.* gradually diminishing until when $p < P$ the *P. D.* becomes reversed, the mercury then comporting itself like zinc or an electro-positive metal. It should here be especially noticed how small a number of ions suffices to determine definitely the *P. D.* between a metal and solution, a consequence of the enormous charges carried by the ions.

Having thus explained the process by which electrical energy may be conceived to be developed at the junction of a metal and liquid, it remains only to throw these ideas into mathematical form. It is evident that we have to consider here an equilibrium between electrical and osmotic or volume energy. A displacement of the one, *e.g.*, by changing the concentration of the solution, produces an equivalent change in the potential of the other. For equilibrium the algebraic sum of all changes in the system produced by any virtual displacement in the equilibrium must be zero. Hence the condition for equilibrium is

$$n_e \epsilon_0 \, d\pi = -v dp$$

where n_e is the valence of the metal in question, ϵ_0 the quantity of electricity carried by a gram-equivalent, $d\pi$ the virtual change in the potential caused by a change dp in the partial osmotic pressure of the kathions, and v the volume in which one gram-equivalent of metal is dissolved. Let π be the unknown *P. D.* between a metal M and a solution in which the partial osmotic pressure of the kathions is p. From our definition of P_M we have seen that $\pi = 0$ when $p = P_M$; hence to find the actual *P. D.* between metal and solution we have simply to integrate the above equation between the limits $\pi = 0$, $\pi = \pi$, and $p = P_M$, $p = p$. The integration is easily performed by the aid of Boyle-van't Hoff's law of solutions

$$pv = RT.$$

Substituting v from this equation in the above we obtain

$$n_e \epsilon_0 \int_0^{\pi} d\pi = -RT \int_P^p \frac{dp}{p}$$

or integrating

$$\pi = \frac{RT}{n_e \epsilon_0} ln \frac{P_M}{p}. \qquad (1)$$

To express π in volts we have only to remember that $R = 1.980$ cal., 1 cal. $= 4.19 \times 10^7$ ergs, and 1 volt $= 10^7$ abs. units, therefore

$$\frac{RT}{\epsilon_0} = \frac{1.980 \times 4.19 \times T}{96540} = 0.860 \, T \times 10^{-4} \text{ volt.}$$

Hence

$$\pi = \frac{0.860}{n_e} T ln \frac{P}{p} \times 10^{-4} \text{ volt.} \qquad (1a)$$

This is the fundamental formula of the theory of the voltaic cell. It expresses the *P. D.* of any reversible electrode as defined on page 330.

The E. M. F. of any constant element or number of elements connected in series is (neglecting the small *P. D.*'s at the liquid junctions) simply the sum of the values of the *P. D.*'s at the several metal-liquid junctions, each calculated by the above formula. Of the quantities P_M and p which enter into this formula we know as yet the value of the former only approximately. Ostwald, who first calculated its value for the more common metals, has drawn a number of interesting and important conclusions regarding it, for the details of which I must refer to his *Lehrbuch*, Vol. II, 1, 948. It may be mentioned, however, that the value of the electrolytic solution pressure of the different metals varies greatly, from about 10^{18} atmospheres for zinc to 10^{-15} atmospheres for mercury. It is for a given metal a characteristic constant, depending on the solvent with which the metal is in contact, as has been recently shown by Jones,[1] and on the temperature and pressure. Its variation with the latter has not as yet been investigated.

For our present purpose, however, we need not consider the value of P_M further, as in all the following experiments the elements or combination of elements are so chosen that P_M is eliminated from the expression for the total E. M. F. Thus the E. M. F. of an element formed of any two reversible electrodes of the same metal is given by the formula

$$E = \frac{RT}{n_e \epsilon_0}\left(ln\,\frac{P_M}{p_2} - ln\,\frac{P_M}{p_1}\right) + \pi',$$

or

$$E = \frac{RT}{n_e \epsilon_0} ln\,\frac{p_1}{p_2} + \pi',$$

where π' is the *P. D.* between the two liquids of the element. That π' may, under certain circumstances, *e. g.*, in certain concentration elements in which acids are employed as electrolytes, have a very appreciable value should not be forgotten. But, as already stated, by proper choice of electrolytes and concentration of the solutions it may usually be reduced to 0.001 volt or less, in which case we can write

$$E = \frac{RT}{n_e \epsilon_0} ln\,\frac{p_1}{p_2}. \qquad (2)$$

The E. M. F. of a constant element with electrodes of the same metal depends, therefore, simply on the relative value of the partial osmotic pressure of the kathions at each electrode. If these two

[1] Jones, Zeitschrift für physikalische Chemie, 14, 346, 1894.

quantities, or quantities proportional to them, can be found, the E. M. F. of the element can be calculated. Now, as osmotic pressure and concentration are proportional at constant temperature, we may take the ratio $\frac{p_1}{p_2}$ as the ratio of the concentration of the kathions at the two electrodes. The whole problem of the cell is thus reduced to finding the kathion concentration at the two electrodes of the cell.

To calculate this for electrodes of the first kind we have in the numerous conductivity and freezing point determinations of electrolytes all necessary data at hand. We have simply to multiply the concentration of the solution by its dissociation to obtain the desired value of p.

With electrodes of the second kind the problem is not quite so simple. Here we must apply Nernst's principles of solubility effect to calculate the number of kathions in solution. These two principles may be stated as follows:

1. In a saturated solution of a partially dissociated substance the active mass of the non-dissociated part is a constant even when a second substance is present in the solution.

2. The product of the active masses of the dissociation products of the substance with which the solution is saturated is also, under all conditions, a constant.

These laws have been tested and verified by Nernst,[1] and particularly by Noyes,[2] by means of solubility experiments. The second law is of the greatest importance in the theory of the cell, electrodes of the second kind finding in it their complete explanation, as our experiments will show. For the simplest case, where both salts, the difficultly soluble one with which the solution is saturated (*i. e.*, the depolarizer) and the added one (the electrolyte), are both binary compounds and both contain an ion in common (we shall always choose this the anion), the above second principle may be expressed as follows:

$$m_0^2 a_0^2 = ma\,(ma + xa_1)$$

where m_0 and a_0 are the solubility and dissociation of the difficultly soluble salt in water alone, m and a its solubility and dissociation in presence of an amount x of the soluble salt whose dissociation is a_1.

[1] Nernst, Zeitschrift für physikalische Chemie, **4**, 372, 1889.

[2] Noyes, ibid., **6**, 241, 1890; **9**, 603, 1892.

Hence to find the kathion concentration of a difficultly soluble salt in presence of a soluble one with identical anion, which evidently is nothing other than our problem of finding p for an electrode of the second kind, we have only to solve the above equation for ma and obtain

$$p = ma = \tfrac{1}{2}\left\{\sqrt{\overline{xa_1}^2 + 4\overline{m_0a_0}^2} - xa_1\right\}, \qquad (3)$$

a formula of which we shall make continual application. It is to be noticed that we have as yet in no way subjected the solubility of the depolarizer to any limitation. Our considerations hold for moderately soluble as well as very difficultly soluble depolarizers. Herein lies the greater generality of our theory over that originally stated by Nernst, the latter being applicable to the case of very slightly soluble (so-called insoluble) salts only.

We have thus reduced the theory of the cell to a simple and calculable basis. The E. M. F. of any constant element with like electrodes is calculable when the ratio of the kathion concentration at the electrodes is known. For the general case, when the electrodes are of different metals, a further knowledge of the electrolytic solution pressure of the metals, a perfectly definite constant capable of experimental determination, is alone necessary. We have now to see how far the theory here developed stands the test of experiment, for it is by this test alone that a theory must stand or fall.

Experimental Investigation.

As my purpose in the present paper is to present in as concise a form as possible the osmotic theory of the cell and the experimental evidence I have obtained in support of it, a detailed account of the experimental part of my investigation can find no place here. For details concerning the apparatus and method used, preparation and form of electrodes and cells, etc., I must therefore refer to the original article, *Zeitschrift für physikalische Chemie*, 13, 590. It may, however, be here mentioned that the E. M. F. of all cells was measured by the well-known null method of Poggendorff, in the special form described by Ostwald.[1] As a measuring instrument I used an exceedingly sensitive capillary electrometer,[2] indicating with certainty

[1] Ostwald, Lehrbuch, 2d ed., II, 1, 811.

[2] Ostwald, Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen, p. 246.

a *P. D.* of 0.0001 volt. All cells were measured in an Ostwald thermostat at 25°. In all cases where the depolarizer was moderately soluble, *e. g.*, thallium chloride, the solutions were saturated with it by rotation in a thermostat at 25° before making up the cells.

The chemicals used were either prepared by myself, or obtained from Kahlbaum and two or three times recrystallized. Special care was necessary in preparing the depolarizers. All solutions were made up to exactly 0.2 equivalent normal either by direct weighing, or, when this was impracticable, by analysis and subsequent dilution.

In order to obtain constant results great care was necessary in the preparation of the electrodes. In all cases (except silver) the electrodes used were in the form of liquid amalgams, prepared by electrolyzing a pure salt of the metal to be used as electrode over a pure mercury kathode. Where both electrodes are of the same metal, liquid amalgam possesses great advantages over solid electrodes, as exact uniformity of surface, a condition on which the *P. D.* to no small extent depends, is easily obtainable with the former, but only with the greatest difficulty with the latter. Although, as is well known, the *P. D.* between an amalgam and solution depends to a small extent on the concentration of the amalgam, by making both electrodes from the same amalgam this ceases to be of effect, the E. M. F. being then quite independent of the absolute concentration. This I proved by special experiments.

Silver cannot be used as amalgam, as its electrolytic solution pressure is very nearly equal to or less than that of mercury. After many fruitless experiments I finally succeeded in preparing equivalent electrodes by depositing a coating of silver from a solution of silver cyanide in potassium cyanide. Electrodes thus prepared when dipped in the same solution of silver nitrate gave against each other an E. M. F. of but 0.0001—0.0002 volt. Conductivity measurements were made by the usual Kohlrausch method at 25°.

Experiments with Moderately Soluble Depolarizers. Thallium Chloride.

In order to test the theory of electrodes of the second kind as developed in the preceding pages, it was necessary to extend the experiments to cells with moderately as well as very difficultly soluble depolarizers. We will first consider the most general and complicated

case, in which the depolarizer is relatively soluble in comparison with the concentration of the electrolyte. It is the establishment of the theory for this case which is of particular importance, as no experiments have to my knowledge been made in this direction. Of the salts which might be used as depolarizers, thallium chloride seemed the best suited for the present purpose, as

First, thallium is a univalent metal, and the equilibrium between thallium chloride and the added soluble chloride is comparatively simple;

Second, the velocity of migration of thallium ions is practically the same as that of potassium and chlorine ions; and

Third, accurate determinations of the solubility of thallium chloride in presence of different amounts of soluble chlorides have been made, furnishing valuable data for a check on our calculation. In order to make use of these data I used solutions exactly similar to those used by Noyes[1] in his solubility experiments, namely, 0.2, 0.1, 0.05, and 0.025 normal.

The first series of experiments was made with cells of the following type:

Tl amalgam.	Saturated solution of TlCl in x KNO_3.	Saturated solution of TlCl in x KCl.	Tl amalgam.

The E. M. F. of this cell is (compare page 338)

$$E = 0.860\ T\ ln\ \frac{p_1}{p_2} \times 10^{-4}\ \text{volt} \qquad (4)$$

where p_1 and p_2 are the partial osmotic pressures or concentrations of the Tl-ions in the potassium nitrate and potassium chloride solutions respectively. The *P. D.* at the junction of the two liquids must in this case be very small, as the velocity of migration of all ions in solution is very nearly equal (that of the NO_3-ion is somewhat less than that of the others), and moreover the total concentration of both solutions is not very different, two conditions both tending to reduce the *P. D.* between the solutions to a minimum. To calculate E from formula (4) it is only necessary to determine the values of p_1 and p_2.

Now p_1, the concentration of the Tl-ions in the potassium nitrate solution, may be assumed equal to the number of Tl-ions in a saturated aqueous solution; for although the solubility of thallium chloride in

[1] Noyes, Zeitschrift für physikalische Chemie, 9, 610, 1892.

potassium nitrate must be slightly increased, as Noyes has shown, yet, the nitrate and chloride being normally dissociated salts, the increase in solubility is due to the formation of thallium nitrate molecules, the number of ions in solution remaining practically constant. If this be true, the conductivity of a nitrate solution saturated with thallium chloride should be equal to the sum of the conductivities of a pure nitrate solution and of a saturated aqueous solution of thallium chloride. That this is the case the measurements given in the following table clearly prove:

TABLE I.

Electrical Conductivity of TlCl and KNO_3 Solutions. (25°.)

Concentration of added KNO_3.	Conductivity of Saturated Solution TlCl.	Conductivity of KNO_3.	Sum of the two.	Conductivity of KNO_3 saturated with TlCl.
0.1	2.045	11.171	13.22	13.23
0.05	....	5.879	7.924	7.921
0.025	....	3.047	5.092	5.095

We may, therefore, put $p_1 = m_0 a_0$, where m_0 is the solubility and a_0 the dissociation of thallium chloride, in water alone. As this is independent of the concentration of the nitrate, which is always taken equal to the concentration of the potassium chloride solution, in order to keep the value of the *P. D.* of the liquid junction a minimum, the numerator of the fraction $\frac{p_1}{p_2}$ is a constant.

On the other hand, p_2, the concentration of the Tl-ions in the potassium chloride solution increases with dilution of the added salt, and therefore the E. M. F. of the cell must diminish. p_2 is to be calculated by the formula

$$p_2 = ma = \tfrac{1}{2}\left\{\sqrt{\overline{xa_1}^2 + 4\,\overline{m_0 a_0}^2} - xa_1\right\},$$

where the letters have the same significance as on page 339. We have here two possibilities open to us. If, as in our experiments, the value of m, the solubility of the depolarizer in presence of the added salt, has been experimentally determined, and a, its dissociation, can by any means be calculated, we have simply to take $p_2 = ma$ in our

calculation. Such solubility determinations are, however, in general wanting, in which case we must calculate p_2 by the solubility principle itself. I have shown in another place that for most practical purposes we may assume for a_1 the value of the dissociation of the added salt (concentration x) in water alone, as calculated from conductivity or freezing point measurements, although, strictly speaking, a_1 is its dissociation in presence of the difficultly soluble salt.[1]

The values of a used in the following calculations are the means of results obtained by three independent methods of calculation.[2] The value of m_0 and m are the mean of Noyes' measurements of the solubility of thallium chloride in potassium and sodium chloride; a_0 is taken equal to 91.3, the most probable value obtained from conductivity and electrometric measurements, and a_1 is calculated both from Kohlrausch's measurements of the conductivity and from Jones'[3] measurements of the freezing point of potassium chloride solutions.

In the following table are the experimental and calculated results on cells with potassium nitrate and potassium chloride as electrolytes, as well as on exactly similar ones with the potassium replaced by the corresponding sodium salts.

TABLE II.

E. M. F. of cells of type I. TlCl as depolarizer. (25°.)

Concentration of the Chloride and Nitrate Solutions.	Obs. E. M. F.; with KCl and KNO_3 as Electrolytes.	Obs. E. M. F.; with NaCl and $NaNO_3$ as Electrolytes.	Mean.	$E=\frac{RT}{\epsilon_0} ln \frac{m_0 a_0}{m a}$	$E=\frac{RT}{\epsilon_0} ln \frac{m_0 a_0}{f_2}$ (a_1 from conductivity).	$E=\frac{RT}{\epsilon_0} ln \frac{m_0 a_0}{f_2}$ (a_1 from freezing point).
0.2	0.0591 0.0588	0.0586 0.0589	0.0589	0.0614	0.0623	0.0619
0.1	0.0443 0.0442 0.0442	0.0439 0.0437	0.0440	0.0452	0.0459	0.0453
0.05	0.0302 0.0300	0.0298 0.0298	0.0299	0.0305	0.0308	0.0301
0.025	0.0179 0.0175	0.0181 0.0180	0.0179	0.0182	0.0183	0.0178

[1] For a discussion of this point, see Zeitschrift für physikalische Chemie, 13, 607, 1894.

[2] Ibid., 13, 613, 1894.

[3] Jones, ibid., 11, 110, 1893.

In the last three columns are the calculated values of E. I have given the results obtained by using in the calculation of p_2 values of a_1, from both freezing point and conductivity measurements, to show the effect of the uncertainty with which we know the value of the dissociation of the added salt on the result. A glance at the last two columns shows this amount to be about 0.0005 volt.

A comparison of the observed values of E with those calculated shows an agreement which must be regarded as satisfactory. The deviations all lie in the direction to be expected from neglecting the possible *P. D.* at the junction of the electrolytes, and in assuming in the calculation of p_2 that a_1 is the same as the dissociation of the added salt in water alone. When one considers the apparently remote connection which the laws of solubility effect, osmotic pressure, and mass action, etc., have with electromotive force, the agreement found in the above table is certainly striking.

It is to be noticed that the predicted decrease of E with increasing dilution is completely verified; further, that replacement of potassium by sodium has no effect whatever on the E. M. F. — a necessary consequence of the theory, as the diminution of the solubility of thallium chloride by all univalent chlorides is the same.

Zinc Chloride and Cadmium Chloride as Electrolytes.

It was further shown by Noyes' solubility experiments that not only do all univalent chlorides diminish the solubility of thallium chloride by the same amount, but also that all bivalent chlorides likewise diminish it by a constant though slightly less amount. Cadmium chloride forms a remarkable exception; addition of this salt diminishes the solubility of thallium chloride only about half as much as does zinc and other bivalent chlorides. Hence, if our theory of the cell is correct, replacement of the sodium and potassium salts in the preceding experiments by equivalent solutions of zinc salts should have the effect of only very slightly diminishing the E. M. F. of the cells. On the other hand, replacement by cadmium salts should diminish the E. M. F. by a very considerable amount.

That the first of these conclusions is completely confirmed by experiment is seen from the following table.

TABLE III.

E. M. F. of Tl, TlCl in $Zn(NO_3)_2$, TlCl in $ZnCl_2$, Tl cells. (25°.)

Concentration of the $Zn(NO_3)_2$ and $ZnCl_2$.	Observed E. M. F.	Mean of Observed E. M. F. of KCl and NaCl cells.
0.2	0.0571	0.0589
0.1	0.0425	0.0440
0.05	0.0290	0.0299
0.025	0.0179	0.0179

The E. M. F. is slightly less than that of the preceding cells, especially in case of the more concentrated ones. That the difference becomes less and less with increasing dilution is due to the fact that the dissociation of the bivalent chlorides more and more nearly approaches that of the univalent chlorides as the concentration decreases.. It is to be noticed that the nature and valence of the soluble kathions, *i. e.*, the Zn-ions, has no influence whatsoever on the E. M. F. It is the concentration and valence of the kathions of the metal used as electrodes alone which affect the E. M. F. of the cell.

The results with cadmium salts are especially interesting. As already stated, I expected a considerable diminution of the E. M. F. on account of the increased solubility, and hence concentration p_2, of the Tl-ions in the chloride solution. Repeated measurements gave, however, always an increase, as is evident from a comparison of the following and preceding tables:

TABLE IV.

Tl, TlCl in $Cd(NO_3)_2$, TlCl in $CdCl_2$, Tl. (25°.)

Concentration.	0.2	0.1	0.05
E. M. F. observed	0.0646	0.0488	0.0327

The cause of this apparent discrepancy between theory and experiment is not far to seek. It lies in the cadmium nitrate solution. We have assumed here, as in our previous experiments, that the concentration of the Tl-ions in the nitrate solution is essentially the same as in an aqueous solution, the reason being in the normal dissociation

of all salts formed in the solution. Now, in the above cadmium nitrate solution this condition no longer holds. Of the four salts formed in solution, thallium chloride, thallium nitrate, and cadmium nitrate are normally dissociated, while cadmium chloride is abnormally little dissociated. The consequence is that if thallium chloride is dissolved in cadmium nitrate the Cd-ions immediately unite with the Cl-ions to form undissociated cadmium chloride, thus causing a diminution of the Cl-ions. As, however, the product Tl-× Cl-ions must remain constant, more thallium chloride must go into solution in order to compensate for this diminution of Cl-ions. The result is an increase in the solubility of thallium chloride and a large preponderance of Tl- over Cl-ions. This increase in the solubility is very considerable. In a 0.2 normal solution the solubility is nearly twice as great as it is in water. A similar abnormal increase in the solubility of this salt was observed by Noyes in a cadmium sulphate solution.

With this fact in mind the explanation of the above results is clear. The increase in the number of Tl-ions in the cadmium chloride solution is more than compensated by a still greater increase in the nitrate solution. The ratio $\frac{P_1}{P_2}$ is, therefore, greater; hence, also, the E. M. F. If this explanation be correct, then a cell formed of a saturated solution of thallium chloride in cadmium nitrate and in zinc nitrate should give an E. M. F., the electrode in the cadmium solution being positive. Experiment fully verifies this prediction, as the following figures show:

TABLE V.

Tl, TlCl in $Cd(NO_3)_2$, TlCl in $Zn(NO_3)_2$, Tl.

Concentration.	0.2	0.1	0.05
E. M. F. observed	0.0142	0.0102	0.0072

The E. M. F. decreases with increasing dilution, as the solubility of the thallium chloride in cadmium nitrate does likewise, while it is practically independent of the concentration of the zinc nitrate. Again, a cell formed with the two chloride solutions should give an

E. M. F., the cadmium solution being positive against the zinc solution, a conclusion likewise verified by experiment, as the following table shows:

TABLE VI.

Tl, TlCl in $CdCl_2$, TlCl in $ZnCl_2$, Tl (25°).

Concentration.	0.2	0.1	0.05
E. M. F. observed	0.0081	0.0047	0.0039

By the aid of the data in the last two tables we can check our previous results on the $Cd(NO_3)_2$ $CdCl_2$ cells. For if p_{ZnCl_2}, $p_{Cd(NO_3)_2}$, etc., be the concentration of the Tl-ions in the zinc chloride, cadmium nitrate, etc., solutions, then

$$C^1 \ln \frac{p_{Zn(NO_3)_2}}{p_{ZnCl_2}} + C \ln \frac{p_{Cd(NO_3)_2}}{p_{Zn(NO_3)_2}} - C \ln \frac{p_{CdCl_2}}{p_{ZnCl_2}} = C \ln \frac{p_{Cd(NO_3)_2}}{p_{CdCl_2}},$$

where the value of the first term is given in Table III, that of the second in Table V, that of the third in Table VI, and that of the last in Table IV. Introducing numerical values we have:

TABLE VII.

Concentration.	E. M. F. Calculated.	E. M. F. Observed.
0.2	0.0571 + 0.0142 − 0.0081 = 0.0632	0.0646
0.1	0.0425 + 0.0102 − 0.0047 = 0.0480	0.0488
0.05	0.0290 + 0.0072 − 0.0039 = 0.0323	0.0327

Considering that the value of the E. M. F. at the junction of the electrolytes has been neglected throughout, the agreement is very satisfactory and confirms our explanation of the above abnormal E. M. F. completely. The above furnishes a pretty example of an apparent discrepancy between experiment and theory which the dissociation theory completely explains, affording thereby far more convincing evidence in favor of the theory than a predicted agreement could have done.

[1] C = constant.

Silver Bromate as Depolarizer.

As further proof of the applicability of our theory to electrodes with moderately soluble depolarizers, I give the following results on a couple of elements in which silver and silver bromate were used as electrodes and depolarizer. The cells were of exactly the same type as those already considered, namely, silver electrodes in saturated solutions of silver bromate in potassium nitrate, and in potassium bromate respectively. The E. M. F. was calculated as before. The solubility m_0 of silver bromate is, according to Noyes, 0.00810. I determined its dissociation by conductivity measurements, and found it to be $a_0 = 94.9$. The values of a_1 for potassium bromate I likewise found to be 83.0 and 87.7 for 0.1 and 0.05 normal solutions respectively. This gives us all data necessary for calculating the E. M. F by formula (3), where, as before, $p_1 = m_0 a_0$, and p_2 is determined from the equation on page 340.

TABLE VIII.

E. M. F. of Ag, $AgBrO_3$ in KNO_3, $AgBrO_3$ in $KBrO_3$, Ag. (25°.)

Concentration of $KBrO_3$ and KNO_3.	Observed E. M. F.	Calculated E. M. F.
0.1	0.0620	0.0612
0.05	0.0471	0.0454

The agreement must be regarded as satisfactory. The deviations lie in the direction to be expected from neglect of the *P. D.* at the liquid junction, due to the unequal velocities of migration of the BrO_3- and NO_3-ions, which, it is easy to see, adds itself to that of the electrodes. The experimental error was somewhat greater here than with the thallium cells, great difficulty being encountered in obtaining exactly equivalent silver electrodes.

Having thus demonstrated the applicability of our theory of electrodes of the second kind to depolarizers of moderate solubility, let us now consider what modification or simplification it admits of when applied to very difficultly soluble depolarizers. It was to this case alone that Nernst's original theory, in which the anions were regarded as the active factor in determining the *P. D.*, applied, and the agreement found both by himself and others between formulæ deduced on

this assumption and experiment makes it of especial importance for us to apply the theory here developed to this same case. We shall see that the formulæ previously obtained by Nernst are simply special cases of those already deduced in the preceding pages.

Experiments with Difficultly Soluble Depolarizers. Theory.

A cell much used in practice on account of its constancy is the well-known calomel element of v. Helmholtz. This consists of zinc in zinc chloride on the one hand, and mercury covered with a layer of calomel in the same electrolyte on the other, or, according to our definitions, of an electrode of the first and one of the second kind. All elements of this type may be expressed by the following scheme:

$$M' \mid M'A \mid \begin{matrix} M''A \text{ (difficultly soluble salt)} \\ \text{in } M'A \text{ (soluble salt)} \end{matrix} \mid M'',$$

and their electromotive force computed by the general formula

$$E = 0.860\ T \left\{ \frac{1}{n_1} ln \frac{P_{M'}}{p_1} - \frac{1}{n_2} ln \frac{P_{M''}}{p'} \right\} 10^{-4} \text{ volt}, \qquad (5)$$

in which n_1 and n_2 are the valences of the metals M' and M'' respectively. Unfortunately, owing to our present meager knowledge of the absolute value of the electrolytic solution pressure of the different metals, the validity of this formula cannot be tested experimentally. Such a test is, however, practicable when we consider two similar cells of different concentration connected in opposition. In this case the observed electromotive force is the difference between the electromotive force of each separate cell, *i. e.*,

$$E = 0.860\ T \left\{ \frac{1}{n_1} ln \frac{P_{M'}}{p_2} - \frac{1}{n_2} ln \frac{P_{M''}}{p''} - \frac{1}{n_1} ln \frac{P_{M'}}{p_1} + \frac{1}{n_2} ln \frac{P_{M''}}{p'} \right\} 10^{-4} \text{ volt},$$

or

$$E = 0.860\ T \left\{ \frac{1}{n_1} ln \frac{p_1}{p_2} + \frac{1}{n_2} ln \frac{p''}{p'} \right\} 10^{-4} \text{ volt}, \qquad (6)$$

where p_1 and p_2 are the partial osmotic pressures (or concentrations) of the M'-ions, p' and p'' of the M''-ions in the first and second cell respectively. The ratio $\frac{p_1}{p_2}$ refers, therefore, to the electrodes of the first kind alone, while $\frac{p''}{p'}$ refers to the electrodes of the second

kind. By this combination of two cells the electrolytic solution pressure of the different electrodes is eliminated, and there remains in the formula for the resulting E. M. F. only quantities which are either known or easily calculated. Thus the ratio $\frac{p_1}{p_2}$ of the kathion concentration of the soluble salt $M'A$ in the two solutions is given directly by the ratio of their electrical conductivities. On the other hand, p' and p'' must in general be separately calculated by the second law of solubility effect. When, however, the depolarizer $M''A$ is very difficultly soluble, or, more precisely, when its solubility is negligible in comparison with the concentration of the soluble salt $M'A$, the calculation of the ratio of the kathion concentration at the electrodes of the second kind becomes greatly simplified. For this special case the general formula (6) may always be reduced to a much simpler form.

Let us consider, for example, two calomel elements connected in opposition. As zinc is bivalent and mercury (in HgCl) univalent, general formula (6) becomes in this case

$$E = 0.860\ T \left\{ \tfrac{1}{2} ln \frac{p_1}{p_2} + ln \frac{p''}{p'} \right\} 10^{-4} \text{ volt.} \qquad (7)$$

As the solubility s of calomel at ordinary temperatures is only about 0.000013 normal, we can assume its dissociation at this extreme dilution to be practically complete. If p_1 is the concentration of the Zn-ions in the more concentrated solution, and therefore $2p_1$ the concentration of the Cl-ions, then p', the concentration of the Hg-ions, by the second solubility principle, will be determined by the equation

$$p'(p' + 2p_1) = s^2,$$

which is the simplified form the general solubility formula assumes under the above conditions. As p' is evidently negligible in comparison with p_1, we obtain the very simple expression for p',

$$p' = \frac{s^2}{2p_1}.$$

Similarly we have for p'' the concentration of the Hg-ions in the diluter solution

$$p'' = \frac{s^2}{2p_2},$$

whence

$$\frac{p''}{p'} = \frac{p_1}{p_2}.$$

That is, *if two calomel elements are connected in opposition, then the ratio of the concentration of the Hg-ions in the first to that in the*

second is the same as the ratio of the concentration of the Zn-ions in the second to that in the first. This proportionality holds true as long as the solubility of the calomel is negligible in comparison with the concentration of the zinc chloride; it is therefore to be regarded only as a limiting case.

Substituting $\frac{p_1}{p_2}$ for $\frac{p''}{p'}$ in (7), we obtain at once the very simple formula

$$E = \frac{3}{2} \times 0.860\ T\ ln\ \frac{p_1}{p_2} \times 10^{-4}\ \text{volt.} \qquad (8)$$

This formula agrees completely with that deduced by Nernst for the same combination of elements, on the assumption that the *P. D.* of electrodes of the second kind is determined by the concentration of the anions and an electrolytic solution pressure characteristic of the depolarizer similar to that which we have assumed for metals. Our theory leads, therefore, to results in no way contradictory to those formerly deduced by the originator of the theory. It is to be regarded rather as a generalization of the older view, all cases like the above, in which the depolarizer belongs to the class of so-called insoluble salts, being only limiting cases of a general theory applicable to depolarizers of all solubilities. The two views are, however, in one respect fundamentally different, for according to Nernst it is the anions which primarily determine the *P. D.*, while according to Ostwald it is the kathions. It is to be noticed that according to the latter view all reversible electrodes are fundamentally the same.

Formula (8) may also be directly deduced (on the assumption that the zinc chloride is completely dissociated) by the principle of virtual energy — a method already used by Ostwald in his treatise on electrochemistry. I give this second proof also, as it is important to see how quite independent considerations lead to the same final result. Let us consider the two calomel elements connected in opposition as a system in which electrical energy and volume energy are in equilibrium with each other. Let the total osmotic pressure in the first (more concentrated) zinc chloride solution be p_1, and in the second p_2; further, let us suppose the amount of zinc chloride so great that no appreciable change of its concentration is caused by the flow of a very small quantity of electricity through the system. If now the circuit be supposed closed just long enough to allow a quantity of electricity $2\,e_0$ to flow through the system, one molecule of

zinc will be dissolved in the diluter solution, while one molecule will be separated out in the more concentrated solution, or, in other words, one molecule of zinc chloride will be carried electrometrically from the more concentrated to the diluter solution. The maximum amount of work to be obtained by this process is evidently

$$-\int_{p_1}^{p_2} v dp.$$

In this expression v, which represents the volume of solution occupied by one gram molecule of zinc chloride, is determined by van't Hoff's equation,

$$p v = i R T.$$

Substituting the value of v from this equation in the above expression for the volume energy, we obtain

$$-RT\int_{p_1}^{p_2} i\frac{dp}{p}.$$

This must be equal to the corresponding electrical energy, *i. e.*, $2\epsilon_0 E$, where E is the electromotive force of the system.

Hence

$$2\epsilon_0 E = -RT\int_{p_1}^{p_2} i\frac{dp}{p}.$$

When the solutions are so dilute that the zinc chloride can be regarded as completely dissociated, $i = 3$, under which condition the integration of the right side of the above equation is at once possible, and we obtain

$$2\epsilon_0 E = 3RT\, ln\frac{p_1}{p_2},$$

or

$$E = \frac{3}{2}\frac{RT}{\epsilon_0} ln\ \frac{p_1}{p_2}. \qquad (9)$$

It is to be especially noticed in this expression for the electromotive force that p_1 and p_2 refer not to the partial osmotic pressure of the kathions, as in formula (8), but to the total osmotic pressure in the two solutions. As, however, the formula holds only for the special case that the zinc chloride is completely dissociated, the ratio of the total osmotic pressure and of the partial osmotic pressure of the kathions in the two solutions is the same; hence for this case (9) and (8) agree completely with each other. When, on the other hand,

the assumption of complete dissociation is inadmissible the above method cannot be well applied. In this case the integration of the expression for the osmotic energy is not easy to carry out, as the value of i as a function of p is not simple. Still less is it applicable to elements with relatively soluble depolarizers. On the other hand, my deduction of formula (7) and (8), in which simply the sum of the potential differences at the various heterogeneous junctions of the elements are considered, is perfectly general, being equally applicable to partially dissociated electrolytes and to soluble depolarizers.

The energy method when applicable has, however, one great advantage, namely, that it has only to do with the final changes produced in the cell. From a consideration of the above deduction of formula (9) it is clear that for the general case, where the zinc is replaced by a metal whose valence is n_e, the zinc chloride by a soluble salt of this metal which dissociates into n_i parts, and the depolarizer by any difficultly soluble salt with an anion in common with the soluble salt, the electromotive force will be given by the formula

$$E = \frac{n_i}{n_e} \frac{RT}{\epsilon_0} ln \frac{p_1}{p_2},$$

or

$$E = \frac{n_i}{n_e} 0.860\ T ln \frac{p_1}{p_2} \times 10^{-4} \text{ volt.} \qquad (10)$$

From this general formula it follows at once that the electromotive force of two elements of the calomel or Clark type joined in opposition depends :

First, on the relative and not on the absolute value of the kathion concentration at the electrodes of the first kind ;

Second, on the valence of the electrodes of the first kind ;

Third, on the number of parts into which the soluble salt (electrolyte) dissociates.

It is, on the other hand, wholly independent of the valence of the electrodes of the second kind and of the depolarizer.

We will now show that the general formula (6) leads to the same results. That such is the case when $n_i = 3$ and $n_e = 2$ we have already seen in our consideration of the calomel elements. Suppose, however, the mercury and calomel in these elements to be replaced by a bivalent metal and its difficultly soluble chloride (unfortunately lead chloride is too soluble at ordinary temperatures to lend

itself to experiment). From the above considerations the electromotive force should remain unchanged. By formula (6), however,

$$E = 0.860\ T \left\{ \frac{1}{2} ln \frac{p_1}{p_2} + \frac{1}{2} ln \frac{p''}{p'} \right\} 10^{-4} \text{ volt}, \qquad (11)$$

which at first sight does not agree with the corresponding formula (7) for calomel elements. It is, however, to be remembered that MCl_2 dissociates according to the scheme

$$M \times Cl \times Cl = s^3.$$

Hence

$$p' (2p' + 2p_1)^2 = s^3,$$

or, neglecting p' in comparison with p_1,

$$p' = \frac{s^3}{4 p_1^2}.$$

Similarly we obtain for p''

$$p'' = \frac{s^3}{4 p_2^2},$$

and hence

$$\frac{p''}{p'} = \left(\frac{p_1}{p_2} \right)^2.$$

Substituting this value of $\frac{p''}{p'}$ in (11) gives at once formula (8), by which the independence of the electromotive force of the valence of the electrodes of the second kind is established as a consequence of (6) as well as of (10).

The valence of the electrodes of the first kind exerts, however, a large influence on the E. M. F. Let us suppose the zinc and zinc chloride replaced by a univalent metal and its soluble chloride or bromide. In this case $n_e = 1$ and $n_i = 2$, hence by (10)

$$E = 2 \times 0.860\ T ln \frac{p_1}{p_2} \times 10^{-4} \text{ volt}. \qquad (12)$$

By (6), on the other hand,

$$E = 0.860\ T \left\{ ln \frac{p_1}{p_2} + ln \frac{p''}{p'} \right\} 10^{-4} \text{ volt}. \qquad (13)$$

In this case p' is evidently to be calculated from the equilibrium equation

$$p' (p' + p_1) = s^2,$$

or

$$p' = \frac{s^2}{p_1}.$$

Hence

$$\frac{p''}{p'} = \frac{p_1}{p_2},$$

which substituted in (13) gives (12). Again general formula (6) agrees with (10) completely.

Let us consider, finally, the influence of the number of parts into which the electrolyte dissociates from the point of view of formula (6). We will suppose the zinc chloride replaced by zinc sulphate, in which case $n_i = 2$ instead of 3. Of course the depolarizer must in this case be a difficultly soluble sulphate. Two cases are here possible, according as the electrode of the second kind is univalent or bivalent, *e.g.*, according as mercurous sulphate or lead sulphate is used as depolarizer. By (10) the E. M. F. should be the same in both cases and given by the formula

$$E = 0.860\ T\ ln\ \frac{p_1}{p_2} \times 10^{-4}\ \text{volt.} \qquad (14)$$

For the first case, when the electrode of the second kind is univalent, formula (6) becomes

$$E = 0.860\ T \left\{ \frac{1}{2}\ ln\ \frac{p_1}{p_2} + ln\ \frac{p''}{p'} \right\} \times 10^{-4}\ \text{volt.} \qquad (15)$$

To calculate p' we have only to remember that Hg_2SO_4 dissociates according to the formula

$$Hg \times Hg \times SO_4 = s^3,$$

and that the concentration of the Zn- and SO_4-ions is the same. Hence

$$p' \times p' \times (p' + p_1) = s^3,$$

from which we get for p'

$$p' = \left(\frac{s^3}{p_1} \right)^{\frac{1}{2}}.$$

Consequently

$$\frac{p''}{p'} = \left(\frac{p_1}{p_2} \right)^{\frac{1}{2}}.$$

Substituting this in (15) we obtain (14), as was to be expected.

For the second case, when the depolarizer is bivalent,

$$E = 0.860\ T \left\{ \frac{1}{2}\ ln\ \frac{p_1}{p_2} + \frac{1}{2}\ ln\ \frac{p''}{p'} \right\} \times 10^{-4}\ \text{volt.} \qquad (16)$$

Here, however, $Pb \times SO_4 = s^2$; hence

$$\frac{p''}{p'} = \frac{p_1}{p_2},$$

which substituted in the above equation leads again to (14).

We have thus shown that formulæ (6) and (10) lead to identical results as long as we assume complete dissociation. Formulæ (8) or (9), (12) and (14), hold, however, quite generally, even when this assumption is no longer admissible, as they are direct consequences of the general formula (6). In them it is to be borne in mind that p_1 and

p_2 are to be taken as the *partial* osmotic pressures (or concentrations) of the kathions, and not as the total osmotic pressure of the solution.

We may sum up the above results as follows:

The electromotive force of two calomel elements connected in opposition is given by formula (8) and will remain unchanged when

1. The mercury and calomel are replaced by silver and silver chloride respectively;

2. The zinc chloride is replaced by zinc bromide or iodide, in which case the depolarizer must be a difficultly soluble bromide or iodide;

3. The zinc chloride is replaced by cadmium chloride.

4. It will, on the other hand, be increased by replacement of the zinc and zinc chloride by a univalent metal, *e.g.*, thallium and its chloride, the electromotive force being given by formula (12); and

5. Diminished, by replacement of the zinc chloride by zinc sulphate. In this case a sulphate must be used as depolarizer, although it is immaterial whether it is of a univalent or bivalent metal, *e.g.*, whether it is Hg_2SO_4 or $PbSO_4$, the E. M. F. being given in either case by (14).

6. If the solubility of the depolarizer is not negligible, then deviations from the above deduced special formulæ are to be expected, and in the direction that the calculated values are too large. The only formula applicable to such cases is the general one (6), in which p' and p'' are each to be separately calculated by the second principle of solubility effect. Cells with thallium chloride as depolarizer should show such deviations from the special formulæ.

Experimental Test of the Theory.[1]

Let us now consider the experimental evidence obtained in support of these conclusions. Measurements were made in a thermostat at 25°, so that all results are directly comparable. The concentration of the electrolyte in the two opposed elements was always taken in the ratio of one to ten, and was varied from 0.2 to 0.001 normal. It is given in the first column of the following tables. In the second and third columns are the observed values of the E. M. F., each the mean of measurements on four combinations of cells. The calculated values are given in the last column of the tables. In the

[1] For details regarding preparation and form of cells, etc., see Zeitschrift für physikalische Chemie, 13, 629, 1894.

calculation of the E. M. F. by formulæ (8), (12), and (14), the ratio $\frac{P_1}{P_2}$ is always taken equal to $\frac{k_1}{k_2}$, where k_1 and k_2 are the electrical conductivities of the respective solutions as determined by Kohlrausch. For convenience the elements will in what follows be designated simply by their soluble salt and depolarizer, thus the two opposed calomel elements as $ZnCl_2$-HgCl elements, etc.

TABLE IX.

E. M. F. of $ZnCl_2$-HgCl and $ZnCl_2$-AgCl Elements. (25°).

Concentration of $ZnCl_2$.	Observed E. M. F. of $ZnCl_2$-HgCl cells.	Observed E. M. F. of $ZnCl_2$-AgCl cells.	E. M. F. calculated by formula (8).
0.2 — 0.02	0.0785 0.0789	0.0765 0.0770	0.0797
0.1 — 0.01	0.0810 0.0790	0.0779 0.0782	0.0818
0.02 — 0.002	0.0847 0.0839	0.0840 0.0845	0.0844
0.01 — 0.001	0.0845 0.0877	0.0844 0.0850	0.0853

In view of the experimental error, which, as is seen, amounted in the above experiments to 0.001 — 0.002 volt, the agreement is very satisfactory. Not only do the $ZnCl_2$-HgCl and $ZnCl_2$-AgCl elements agree throughout with each other, whereby conclusion 1 is verified, but also the agreement of both with the calculated values is good. It is to be noticed that the E. M. F. is not absolutely independent of the concentration of the zinc chloride; it increases somewhat with increasing dilution. This is, however, in perfect agreement with the theory when the increasing dissociation of the zinc chloride (which increases from 69 per cent. at 0.2 to 96 per cent. at 0.001 normal) is taken into account. The calculated values show the effect of this increase clearly, and the good agreement between them and the observed values is striking proof that it is the partial osmotic pressure or concentration of the kathions and not the absolute concentration of the solution which is the effective factor in determining the electromotive force.

In Table X are the results of the measurements made to test conclusion 2. A second series on $ZnBr_2$-AgBr cells was also carried out to further test conclusion 1. These cells were very constant,

measurements extending over several days showing variations of hardly 0.001 volt. In the calculation the dissociation of zinc bromide is assumed equal to that of the chloride, the conductivity of the bromide not having been determined.

TABLE X.

E. M. F. of $ZnBr_2$-HgBr and $ZnBr_2$-AgBr cells. (25°.)

Concentration of $ZnBr_2$.	Observed E. M. F. of $ZnBr_2$-HgBr cells.	Observed E M. F. of $ZnBr_2$-AgBr cells.	E. M. F. calculated by formula (8).
0.2 — 0.02	0.0797 0.0789	0.0793	0.0797
0.1 — 0.01	0.0795 0.0820	0.0802	0.0818
0.02 — 0.002	0.0863 0.0856	0.0852	0.0844
0.01 — 0.001	0.0866 0.0859	0.0858	0.0853

A glance at the table shows again a complete confirmation of conclusions 1 and 2. A comparison of the second and third columns with the corresponding ones in Table IX shows that the E. M. F. of all four different cells differs, on an average, scarcely 0.001 volt from the theoretical values.

The experiments in which zinc was replaced by cadmium are especially interesting. In the second column of Table XI are the observed values of the E. M. F. on $CdCl_2$-HgCl cells, each the mean of six or eight independent measurements. In the third column are the results of a second series of measurements on $CdCl_2$-AgCl cells, which were made in order to ascertain whether the disagreement observed with the $CdCl_2$-HgCl cells was due to experimental error or whether it was a real discrepancy between experiment and theory.

TABLE XI.

E. M. F. of $CdCl_2$-HgCl and $CdCl_2$-AgCl cells. (25°.)

Concentration of $CdCl_2$.	Observed E. M. F. of $CdCl_2$-HgCl cells.	Observed E. M. F. of $CdCl_2$-AgCl cells.	E. M. F. calculated.
0.2 — 0.02	0.0584	0.0576	0.0657
0.1 — 0.01	0.0634	0.0621	0.0695
0.02 — 0.002	0.0747	0.0760	0.0771
0.01 — 0.002	0.0801	0.0794	0.0794

It was to be expected that the calculated values (column 4) would differ somewhat from those for zinc chloride cells, as cadmium chloride is, as is well known, abnormally dissociated. They are, in fact, throughout somewhat smaller. I did, however, expect an agreement between these values and the observed. This, however, was found only for the diluter solutions. The observed E. M. F. of the first two cells was much too small by about 0.008 volt, an amount far greater than the experimental error. Moreover, repeated measurements always gave the same result and the $CdCl_2$-AgCl cells showed the same deviations.

The explanation of this seeming discrepancy is not far to seek. It lies in the fact that in relatively concentrated solutions cadmium chloride dissociates not only into Cd- and Cl-ions, but also into CdCl-ions. Now, the *P. D.* of the electrodes of the first kind is determined by the concentration of the Cd-ions alone, and of the electrodes of the second kind indirectly by that of the Cl-ions, the CdCl-ions having no influence whatever on either electrode. The conductivity is, on the other hand, dependent on all three kinds of ions. When it is further borne in mind that with increasing dilution the dissociation goes more and more completely over into three ions, and hence the electrical conductivity gives a more and more correct measure of the dissociation into Cd- and Cl-ions, a slight consideration will show that for concentrated solutions the E. M. F. as calculated above must of necessity be too high. For dilute solutions alone, in which a minimum number of CdCl-ions are present, is an agreement between calculation and observation to be expected. A glance at Table XI shows this to be the case.

This conclusion regarding the nature of the dissociation of cadmium chloride to which our E. M. F. measurements lead us is further confirmed by a comparison of the values of the dissociation calculated from conductivity and freezing point[1] measurements, which for concentrated solutions differ widely. We have thus in E. M. F. measurements of reversible cells a selective method leading to a direct determination of the concentration of particular ions, the kathions (and indirectly anions), in solution, a method which will doubtless find extensive application to various problems in the theory of solutions and chemical equilibrium.

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[1] See Zeitschrift für physikalische Chemie, 13, 633.

Returning now to the problem before us, let us consider the results obtained by replacing zinc by a univalent metal by which the E. M. F. should by 4 (page 357) be increased. The only univalent metal which possesses a sufficiently soluble chloride, and which at the same time can be used as electrode, is thallium. For electrolytes I prepared a saturated solution of thallium chloride at 25°, which was then in part diluted to a half, a tenth, and a twentieth of its concentration. Calomel was used as depolarizer. The results are given in the following table. The values given in the last column are calculated by formula (12), the dissociation of the four thallium solutions being taken as 91.3, 95, 98, and 100[1].

TABLE XII.

E. M. F. of TlCl-HgCl cells. (25°.)

Concentration of TlCl.	Observed E. M. F.	Calculated E. M. F.
0.0161 — 0.00161	0.102	0.114
0.008 — 0.0008	0.100	0.115
0.0161 — 0.008	0.0328	0.033

The E. M. F. is, as predicted, considerably greater than that observed with the corresponding zinc cells, having increased from about 0.08 volt to 0.10 volt. The agreement with the calculated values is, however, only approximate, at least in the first two cases. The reason for this is, I believe, to be found in the fact that thallium decomposes water even in the cold to a slight extent, the result of which is that the concentration of the Tl-ions in the immediate neighborhood of the electrodes is greater than that in the solution as a whole. As the relative increase in the concentration of the Tl-ions would be greater in the diluter of the two solutions, the effect must be to slightly diminish the E. M. F. This explanation is borne out by the fact that these cells were very sensitive to the slightest jarring. The experimental error was for this reason much larger than in any of the preceding cells, amounting here to 0.003 — 0.006 volt. That the E. M. F. of our previously investigated thallium

[1] The last three values are estimated and are to be considered as only approximate.

cells was constant is explained by the fact that the solutions were saturated with thallium chloride, and hence (practically) for every molecule of thallium hydrate formed a molecule of thallium chloride separated out, the total concentration of the Tl-ions thus remaining unchanged.

In the following table are the results obtained, showing the effect of the number of ions into which the electrolyte dissociates on the E. M. F. Replacing zinc chloride by zinc sulphate, n_i becomes 2 instead of 3, whereby the E. M. F. should be less than that observed in Tables IX, X, and XI. It should, moreover, be only one half that observed in the case of thallium chloride as electrolyte, for which $n_i = 1$. These conclusions are fully confirmed by the measurements given in the following table.

TABLE XIII.

E. M. F. of $ZnSO_4$-$PbSO_4$ cells. (25°.)

Concentration of $ZnSO_4$.	Observed E. M. F.	Calculated E. M. F.
0.2 — 0.02	0.0421 0.0433	0.0453
0.1 — 0.01	0.0436 0.0445	0.0471
0.02 — 0.002	0.0519 0.0525	0.0500

The agreement with the theoretical values calculated by (14) is also satisfactory. The experimental error amounted in this case to about 0.002 volt between individual cells. The E. M. F. did not become constant until about an hour after preparing the elements, due, doubtless, to the somewhat greater solubility of lead sulphate.

As further proof of the independence of the E. M. F. of the depolarizer, I give two measurements on cells exactly similar to the preceding, with the lead and lead sulphate replated by mercury and mercurous sulphate, *i. e.*, cells no other than the well-known Clark cells. Unfortunately, owing to the tendency of mercurous sulphate to form basic salts, the E. M. F. of these cells proved very inconstant, falling off rapidly and irregularly. I give, therefore, only approximate values taken directly after setting up the cells and after twenty-four hours.

TABLE XIV.

E. M. F. of $ZnSO_4$-Hg_2SO_4 cells. (25°.)

Concentration of $ZnSO_4$.	Observed E. M. F.	Calculated E. M. F.
0.2 — 0.02	0.047 — 0.034	0.045
0.1 — 0.01	0.045 — 0.033	0.047

The first values agree very well with the theoretical, showing them to represent the true E. M. F. of the cells before the depolarizer becomes contaminated with basic salt, the formation of which is indicated by the depolarizer gradually turning yellow. It is clearly evident from the last two tables that the valence of the electrode of the second kind is without influence on the E. M. F., as our theory requires.

In all cells thus far considered a salt has been chosen as depolarizer whose solubility was negligible in comparison with the concentration of the electrolyte. Let us now see the effect on the electromotive force when this condition no longer holds. Our theory requires, as stated in conclusion 6 (page 357), that the E. M. F. should be less than that calculated by the special formulæ — that, in other words, these no longer hold, and we must go back to general formula (6) in order to calculate the E. M. F. of the cell.

To test this conclusion I chose thallium chloride as depolarizer, the solutions of zinc chloride being saturated with this salt previous to setting up the cells, as in the first experiments described in this paper. The cells corresponded exactly to the calomel cells already investigated, with the single difference that mercury was replaced by thallium. The E. M. F. was very constant. The results are given in column 2 of the following table.

TABLE XV.

E. M. F. of $ZnCl_2$-TlCl cells. (25°.)

Concentration of $ZnCl_2$.	Observed E. M. F.	E. M. F., calculated by (6).	$\frac{1}{2}\frac{RT}{\epsilon_0} ln \frac{p_1}{p_2}$	$\frac{RT}{\epsilon_0} ln \frac{p''}{p'}$	Sum.
0.2 — 0.02	0.0679	0.0797	0.0266	0.0431	0.0697
0.1 — 0.01	0.0615	0.0818	0.0272	0.0348	0.0620
0.02 — 0.002	0.0441	0.0844	0.0281	0.0124	0.0405
0.01 — 0.001	0.0339	0.0853	0.0284	0.0066	0.0350

A glance at columns 2 and 3 shows at once the predicted deviation between observed values and those calculated from special formula (8). The deviation is nearly 0.01 volt even for the most concentrated solution, and increases rapidly with increasing dilution. This was *a priori* to be expected, for, as we have seen, the solubility of the thallium chloride in a soluble chloride increases rapidly as the concentration of the latter diminishes, whereby the condition under which formula (8) was deduced, namely, that the solubility of the depolarizer is negligible, becomes less and less fulfilled. Let us see now if the general formula (6) leads to correct results. For the above case it takes the form

$$E = \frac{1}{2}\frac{RT}{\epsilon_0} ln \frac{p_1}{p_2} + \frac{RT}{\epsilon_0} ln \frac{p''}{p'}.$$

In the fourth column is given the value of

$$\frac{1}{2}\frac{RT}{\epsilon_0} ln \frac{p_1}{p_2},$$

i. e., that part of the total E. M. F. arising from the electrodes of the first kind. In the fifth column is given the value of

$$\frac{RT}{\epsilon_0} ln \frac{p''}{p'},$$

that part of the E. M. F. due to the electrodes of the second kind. The quantities p' and p'' are each calculated by formula (3), page 340, in which $a_0 = 91.3$ and a_1 equal to the dissociation of zinc chloride as calculated from Kohlrausch's conductivity measurements.

The results are very significant. In the first place it is seen that that part of the E. M. F. arising from the electrodes of the first kind is practically independent of the concentration, while that arising from the electrodes of the second kind is directly dependent. Moreover, it is easy to see that with increasing dilution this latter part rapidly approaches the limiting value zero, while with decreasing dilution it approaches the value

$$\frac{RT}{\epsilon_0} ln \frac{p_1}{p_2} = 0.0532 \text{ volt.}$$

The last column contains the sum of columns 4 and 5, which should be the true calculated value of the E. M. F., and, in fact, a comparison with column 2 shows an agreement wholly satisfactory. This last series of experiments furnishes a most striking confirmation of our theory; not only are we able to predict when deviations from our

special formulæ should occur, but also, and this is more important, we are able to calculate the exact amount of such deviations.

It is interesting to investigate just what relation must hold between the solubility of the depolarizer and the concentration of the electrolyte in order that our special formulæ may be applicable. Let us consider the above case.

Writing formula (8) for short

$$E = C \ln \frac{p_1}{p_2},$$

it is evident that an error δp in p_1 or p_2 will cause an error

$$\Delta E = C \frac{\delta p}{p},$$

in the observed E. M. F. If now we assume the experimental error in E to be $\Delta E = 0.001$ volt, which, as we have seen, is about the mean error in the above experiments, and $C = 0.0256$ (its value at 25°), then the maximum allowable fractional error in p is equal to 0.039, or, in other words, an error in p which does not exceed 4 per cent. may be neglected. Let s be the solubility of the depolarizer and p the concentration of the soluble salt, which we will assume to be completely dissociated. If, as in the above case, the depolarizer is a binary salt,

$$p' = \frac{1}{2}\left(\sqrt{p^2 + 4s^2} - p\right),$$

or, expanding by the Binomial theorem and simplifying,

$$p' = \frac{s^2}{p}\left(1 - \frac{s^2}{p^2} + \ldots\ldots\right).$$

If, therefore,

$$\frac{s^2}{p^2} \leqq 0.04,$$

we may assume $p' = \frac{s^2}{p}$ without introducing an error in E greater than 0.001 volt, and hence the special formulæ are applicable.

In the first (most concentrated) of the last considered $ZnCl_2$-TlCl cells, $s = 0.016$, $p = 0.02$, from which $\frac{s^2}{p^2} = 0.6$; hence the inapplicability of formula (8) was to be expected.

A very pretty confirmation of the above conclusion is the follow-

ing. The solubility of thallium bromide I found to be 0.0020 normal at 25°; hence

$$\frac{s^2}{P^2} = \frac{\overline{0.0020}^2}{\overline{0.02}^2} = 0.01.$$

Thallium bromide may, therefore, be regarded as a difficultly soluble depolarizer (*i. e.*, the special formulæ are applicable) as long as the concentration of the soluble bromide in which it is dissolved is not much less 0.02 normal. If, therefore, the thallium chloride and zinc chloride in the last considered cell are replaced by thallium bromide and zinc bromide (0.2 — 0.02 normal), the same E. M. F. is to be expected as we have already found using calomel, mercurous bromide, silver chloride, and silver bromide as depolarizers, namely, 0.0799 volt. As a matter of fact, I actually found for this cell 0.0792 volt.

Other experiments at once present themselves which might serve to further test our theory, but I think the above will suffice to establish beyond a doubt its general applicability. The preceding experiments have been particularly chosen to establish the theory of electrodes of the second kind and the generality of the law that the *P. D.* between a metal and liquid is determined primarily by a characteristic constant of the metal and by the concentration of the kathions, be this great or exceedingly small. The *P. D.* of electrodes of the first and second kind is given by the same fundamental formula, the sole difference between them being in the method of calculation of the kathion concentration. This concentration for the former may be determined at once by any of the well-known methods of determining electrolytic dissociation, *i. e.*, conductivity, freezing point methods, etc., while to determine it for the latter Nernst's second principle of solubility effect must be applied. The anions, it will be seen, have no direct influence on the E. M. F.; only in the case of electrodes of the second kind do they play a secondary rôle in determining according to the laws of mass action the concentration of the kathions. The E. M. F. of a reversible element may be said, therefore, to be independent of the anions.[1]

ROGERS LABORATORY OF PHYSICS,
September, 1894.

[1] Quite recently a very striking experimental proof of this conclusion, extending to twenty-three different anions, has appeared in a paper by Neumann, Zeitschrift für physikalische Chemie, **14**, 193, 1894.

SUMMER INSTRUCTION AT THE INSTITUTE.

FROM the foundation of the "School of Industrial Science," classroom and laboratory exercises have been abundantly supplemented by excursions for the examination of such material — mines, manufactories, buildings, geological formations — as could not otherwise be directly studied. Very early in the history of the Institute some of these excursions grew into summer schools, at first for visits to more or less remote mining regions, later for extended practice in civil engineering operations. The following account of last year's schools shows the present scope and character of this work, as well as its more recent developments. A summer school of Naval Architecture will be held for the first time this year.

THE SUMMER SCHOOL OF TOPOGRAPHY, GEODESY, AND GEOLOGY.

In June, 1894, eighteen students from the third year class in Civil Engineering attended the optional summer course in surveying. The school was held in the northeastern section of the Adirondack region in New York, near Keeseville, the same locality that was found so admirably adapted to the fieldwork of the school the previous year.

The instruction was under the charge of Professor Burton, Professor Porter, and Mr. Robbins, of the Civil Engineering Department, and Messrs. Nichols and Stose, of the Geological Department of the Institute. The only work of a geodetic character attempted this year was a series of experiments in base-line measurement. The apparatus used was not essentially different from that of the previous year, except that in place of the electrical device for determining the temperature of the tape a 100-meter brass tape was used, in conjunction with the 100-meter steel tape, and the temperatures of the tapes were determined from the different rates of expansion of the two metals, on the principle of the metallic thermometer. A novel feature of the work this year was the use of the apparatus at night. A series of four measurements of nearly a kilometer of the base line, two with

the brass and two with the steel tape was made at night between the hours of 11.30 P.M. and 4 A.M. The actual difference between the two measurements of the steel tape, after correcting for temperature, was but one seven hundred and fifty thousandth of the length of the line measured. The probable error derived from the comparison of all the different measurements made of the same line would place this part of the school work on a par with like measurements of base-lines made by the Missouri River Commission and the United States Coast and Geodetic Survey. The degree of precision attained was far greater than was necessary for the triangulation used in the topographical survey of the surrounding region, and the reason for expending so much care and time on this work was mainly for the purpose of instructing students in the methods of geodetic measurement. Every student entered into this work with enthusiasm. The singleness of purpose with which each man carried out his assigned duty, having a fixed determination to do his best, is worthy of much praise.

The precise level lately purchased by the Institute was used in running a short line along the banks of the Au Sable River in order to determine the average fall of the river.

The triangulation stations established the previous year were used in continuing the topographical work with the plane-table. The map, which is on the scale of 600 feet to the inch, with contours 10 feet apart, was extended over an additional area of sixteen hundred acres. The locality is peculiarly well adapted for instruction in plane-tabling, and the student here obtains a knowledge of topographical methods which it is utterly impossible to impart during the regular Institute course in Boston.

Soundings were taken in the south arm of Auger Lake, thus completing the hydrographic survey of the bottom of this lake begun the previous year.

The hydraulic fieldwork of the school consisted in the measurement of the discharge of the Au Sable River at two different points, and of the discharge of a mill-flume at Keeseville. The measurements were made by means of floats and current meters. The use of the Darcy tube was made for the first time this year. The Ritchie-Haskell meter was rated by rowing between fixed points on the lake.

The principal feature of the geological fieldwork was the construction of a geological profile eight miles long, from the western bank of the Au Sable River to the shore of Lake Champlain, the line

running in a general direction of South 70° East. Distances and elevations along this line were determined by the use of the transit and stadia. Two independent lines were run side by side over the whole distance, thus furnishing a satisfactory check of the measurements at the close of the work. After plotting this work to scale, the geological features were studied in the field and properly located on the paper, under the direction of the instructors in geology. In addition to the construction of this section, which in itself is especially interesting on account of the many lake and river terraces included in the district, the geological fieldwork included many interesting excursions in search of minerals and fossils to mines, quarries, and the famous Au Sable chasm.

Although the weather was by no means uniformly favorable to the work during the month of June, yet there were few interruptions in the prearranged programme, and the total amount accomplished exceeded that of the previous year. The health of the party was generally good, and a spirit of cheerfulness and satisfaction seemed to prevail.

In conclusion it may be well to say that a pleasant feature of our half holiday was a well-earned victory of our baseball players over the local talent of Keeseville.

THE SUMMER SCHOOL OF MINING.

The Summer School of Mines for the students in Mining Engineering at the Institute of Technology was held in 1894 in Nova Scotia and Cape Breton, and, according to the usual general plan, included the four main divisions of mine work, namely, underground and surface work, and surveying above and below ground. One week was spent at the mines of the West Waverly Gold Mining Company, of Nova Scotia. The students received their general introduction to mining, milling, and surveying. The freedom of the mine and works was given to the party, and many valuable points were picked up by the members, thanks to the generous hospitality of Mr. Hardman, the general manager.

Three weeks were spent in Cape Breton, where the students were the guests of the Dominion Coal Company, of which the Hon. David Mackeen is general manager. The party was here divided to gain the best results, one squad going with Prof. H. O. Hofman and

Mr. J. P. Lyon, for underground work of all kinds, to the Gowry Colliery, of Cow Bay, of which Mr. A. M. Evans is superintendent; the other camping out with Professor Richards near the Victoria mines, of which Mr. T. J. Brown is superintendent.

The Dominion Coal Company had a problem to solve in regard to which there has been some controversy, namely — Is the Mullins coal seam on Sydney Harbor the same as the Lingan seam of Indian Bay? Messrs. Robb and Fletcher, of the Canadian Geological Survey, as well as Mr. Brown, claimed that these were not identical, while some local mining men claimed that they were the same. This problem looked full of difficult points to be determined, and was, therefore, so attractive that it was undertaken, although much too extensive for the short time that could be given to it. From the data obtained, the accompanying map was made as a contribution towards the solution of this problem.

In the survey, the members of the party worked in pairs, and only such work as gave evidence of being correct was accepted for the map. The error referred to at Station 17, which crept in in spite of watchfulness, was due to a misuse of one of the instruments, whereby three miles of map, from Station 17 to 33, had to be condemned. Later, when this work was repeated, it was found that some small boys had removed all the stakes, and, unfortunately, the map had not quite enough secondary check points to make good the loss. The error, however, affects the computations to a small degree only.

The thickness of the coal seams was measured by foot-rule; that of the rock strata determined by measuring the distance upon the map at right angles to the strike between the important rocks, and multiplying this by the sine of the angle of dip. By this method a complete section of coal and rock thickness was obtained for the Victoria shore on the south side of the entrance to Sydney Harbor, from the Mullins seam to Low Point Light as far as the exposures could be seen, and also a second section on the Atlantic shore from Low Point Light around into Indian Bay. These two sections will be found drawn to scale, side by side upon the map. The coal seams are plotted in, according to the position of the seam at high water level. For example, the place given on the map for a seam on a hill will be to the north of the point on the ground, since the coal dips that way.

The standard line of reference for the outcrops of the coal seam

was the Ross or David's Head seam. This seam has been thoroughly proved, and for placing it on the map, the Victoria shore outcrop, the old and new Victoria mines, the Barasois Brook outcrop, the Ellwood, Ribby, and Grace farms, and the David's Head shore outcrop were available. Using this line as a basis, the other seams were drawn approximately parallel to it, widening the space when the dip was light, narrowing it when the dip was heavy, the outcrops on the shore, etc., being used as starting points from which to draw the lines.

In regard to the Lingan seam there were but two locations made, that in Indian Bay and that in Barasois Brook. The assumption that the Hugh McGilvary seam and the little one below it on the Victoria shore correspond to the Lingan seam is based, first, upon the fact that the Lingan seam has a clay parting in it, widening rapidly toward the west; and, secondly, that the Hugh McGilvary seam does not seem large enough to correspond alone to the Lingan. With this assumption, the Victoria section and Lingan section agree very well both as to their larger and smaller seams.

The Mullins seam was located at two points — one on the shore, one on the hill about a mile away. The remarkable change of dip, from 35° on the shore to 10° on the hill, makes it impossible to predict where the high water line on this seam will be. The assumption is made that the average of 10° and 35° will be the dip at the shaft on the hill, and the high water line level is drawn accordingly.

In regard to the problem to be solved, namely — Are the Lingan and Mullins seams identical? we know, first, that the Lingan seam plots all right to the Hugh McGilvary seam; secondly, that under the Lingan seam there are a few little seams, including one of about $2\frac{1}{2}$ feet of coal, which correspond to a similar group under the Hugh McGilvary seam; and, thirdly, under both groups there is a very thick bed of shaly sandstone. This was measured on the Victoria side to be 1,018 feet thick; on the Lingan side no measure could be made for lack of time, but the logic of the situation is quite clear. If the Lingan section agrees substantially with the Victoria section down to the Lingan seam, is it not probable that it will continue to do so, making the layer of sandy shale on the Lingan section as thick as its counterpart on the Victoria section?

Now, the Paddy Ryan seam, which is some three miles inland from the Lingan shore outcrop, may very well be the eastern counterpart of the Mullins seam, for the sandy shale, which is only about three

fourths of a mile from foot to hanging wall on the Victoria shore, where its dip is 35°, could, with no more thickness of strata, cover the distance of three miles at a dip varying from 13°, which it is at Lingan, to 2°, which is reported for Paddy Ryan seam, the exact dip required for a stratum 1,018 feet thick to cover three miles being 3° 41′. It may be said, then, that all the data obtained point towards the Paddy Ryan and Mullins seams being identical, while it is clearly proved that the Lingan is not the same as the Mullins.

Among the valuable experiences gained by the mining students in the Summer Schools of Mines, this experience in working out stratigraphical problems of veins and seams ranks very high. It gives him the practice in predicting where to look for ore and coal deposits, which is an important part of a mining engineer's duties. The experience in plane-table surveying is a great help to the students in two ways: it gives the student in the general mining course this handy, rapid method of making a map — for which the Institute course cannot provide — and it is of special value to the metallurgical student, because he here gains the principles of surveying, which are of necessity omitted from his course.

The party met with the warmest and kindest reception from the officers of the Dominion Coal Company, among whom should be especially mentioned Messrs. David Mackeen, J. W. Revere, J. S. McLennan, T. J. Brown, and A. M. Evans. Every facility was afforded to the party, although the company was hampered at the time by the construction of its new works.

THE SUMMER SCHOOL OF ARCHITECTURE.

Among European architectural clubs and associations the custom of spending a part of each season in short excursions to different towns and buildings of historical and architectural interest has been adopted for many years. Arranged necessarily in the summer months, these trips afford a most welcome relief from the confining duties of professional practice.

To the architectural student such visits are of the greatest value. The pleasure and benefit derived from the close examination of actual structures, from the solution of the numerous questions which arise in efforts to trace the effects of peculiarities of plan and detail, and especially from the spirit of good fellowship which always prevails in these

Victoria Areas
OF THE
Dominion Coal Co.

MAP SHOWING THE SHORE LINE AND COAL SEAMS AT HIGH WATER LEVEL.

Surveyed By The Students Of The
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
JUNE 1894.

This map is believed to be in the main accurate although little has been done in the way of checks. One error is known to exist at Station 17; The map to the westward has probably swung a little upon station 17 as a pivot. The error is not large enough however to seriously injure the computations, Extreme shortness of time is our apology for handing in a map known to have an error. The total time on the ground netted ten working days.

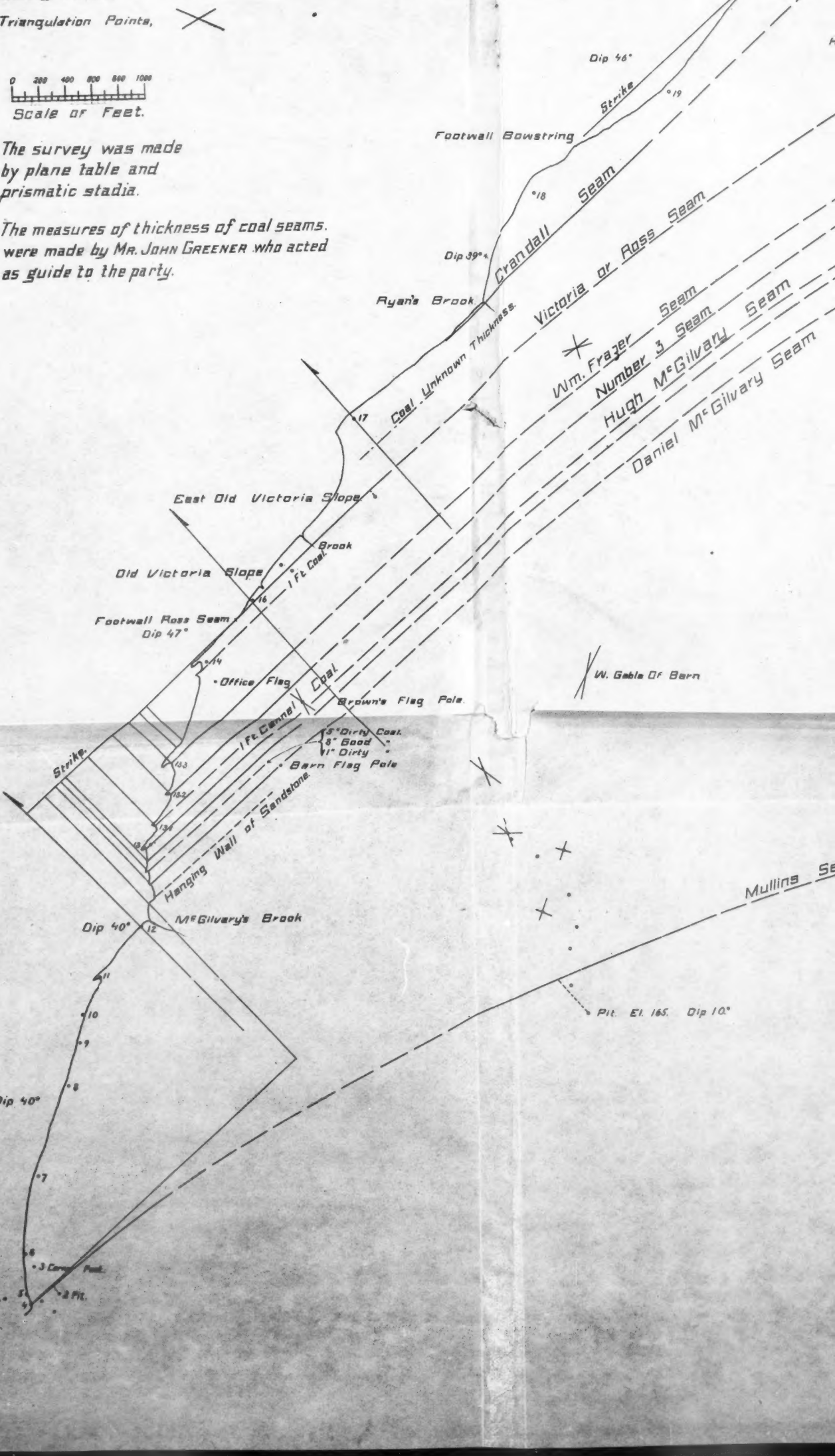
W.P. Anderson.
A.S. Coburn.
B. Hodge.
E.C. Jacobs.
R.H. Lewis
C.E. Locke.
G. Moore.
C.S. Newhall.
M.A. Sears.
B. Stoughton.
C.R. Walker, Del.
R.H. Richards,
In Charge of Party.

Strikes of Strata, 42 ——— 42
Survey Points, 12 •
Triangulation Points, ×

0 200 400 600 800 1000
Scale of Feet.

The survey was made by plane table and prismatic stadia.

The measures of thickness of coal seams. were made by Mr. John Greener who acted as guide to the party.



LOW POINT LIGHT

29 30

28

Ledges Outcrop At Low Tide.

Ledges Outcrop At Low Tide.

Great Slide

Sunken Ledges Dip 12½°

33.3 35 35.1 32 33.1 33 33.2 34

Hanging Wall Sandy Shale

6" Under Footwall Clay Shale

33.2 - Footwall Red Clay Shale

33.1 - Footwall Hard Shale

27

Clay Bottom

Covered With Pebbles

Carr Seam

Keef Seam

McNeil Seam

26

26A

26B

23

Paint Seam

Footwall Great Ledge

Footwall Top Seam 24

21

Flag Pole.

N. Gable Barn.

Brook.

20

Square Stack — Stacks

Hanging Wall of Outcrop — Centers of Three Slopes Victoria Mines. El. 86

Seam

ary Seam

Mullins Seam

Great Slide

Outcrop

Outcrop

DIP 16°

Spring, probable outcrop of Keef Seam

Hanging Wall Sandy Shale

Under Footwall Clay Shale

Footwall Red Clay Shale

Hard Shale

N. Chimney McNeil's Yellow House

N. Gable McNeil's

1 Ft. Seam about here

Dip 14°

Barasois Seam

Dunphy Seam

Pit. El. 98

Bore Hole

Pit.

Camp.

8 Inch Seam

Brook

Pit.

Slope

Brook

Dip 12°

Dip 18°

Dip 18°

ELLWOOD'S BROOK

RIBBY BROOK

GRACE'S BROOK

Grace's Brook Seam

David Head Seam

Ribby Chimney

Pit El. 42.9

J. Connor's Barn E. Gable

Ribby's Old Shaft El. 33.4

Ribby's New Shaft El. 36.5

Fairy House Seam

Northern Head Sea

Pit El. 70.5

M. Connor's House

Lingan Seam

2' 9" Seam

Victoria Section & Lingan Section.

COAL 2.5 ft.

ROCK 144.

COAL 0.5 ft.
CLAY 0.5 ft.
COAL 2 ft.

ROCK-23

COAL 3.5 ft.

ROCK Incl.
338.

Paint Seam..... COAL 3 ft.
CLAY 3 ft.
COAL 4 ft.

ROCK 252.9

COAL 0.5 ft.
CLAY 2.5 ft.
COAL 6 ft.

ROCK 55.

COAL 3.0 ft.

ROCK-23.2

Crandall Seam--COAL 4 ft.-?

COAL 0.7 ft.

ROCK Incl.
283.

ROCK 276.2
One or two small seams

Ross Seam.....COAL 7.0 ft.
ROCK 40.1 ft.
COAL 1.0 ft.

COAL 7 ft.
ROCK 30
COAL 2.4

ROCK 268.1 ft.

ROCK 25

COAL 2.0 ft.

COAL 3.5 ft.
ROCK 66.4
COAL 5.0 ft.

ROCK 103.6 ft.

ROCK 67.1

Number 3 Seam--COAL 5.0 ft.

COAL 1.5 ft.

ROCK 69.8 ft.

ROCK 44.4

COAL 1.0 ft.

COAL 8.0 ft.

ROCK 35.7 ft.

Hugh McGilvery Seam COAL 4.8 ft.

ROCK 81.7

ROCK 48.2 ft.

COAL 1.2 ft.

COAL 6.0 ft.

ROCK 32.2 ft.

ROCK 44.7

COAL 1.9 ft.

COAL 0.85

ROCK 52.5 ft.

COAL 0.5

Daniel McGilvery..... COAL 2.2 ft.
ROCK 13.0 ft.
COAL 0.5 ft.

+ Clay - 1.0

Then ROCK

" COAL

" ROCK

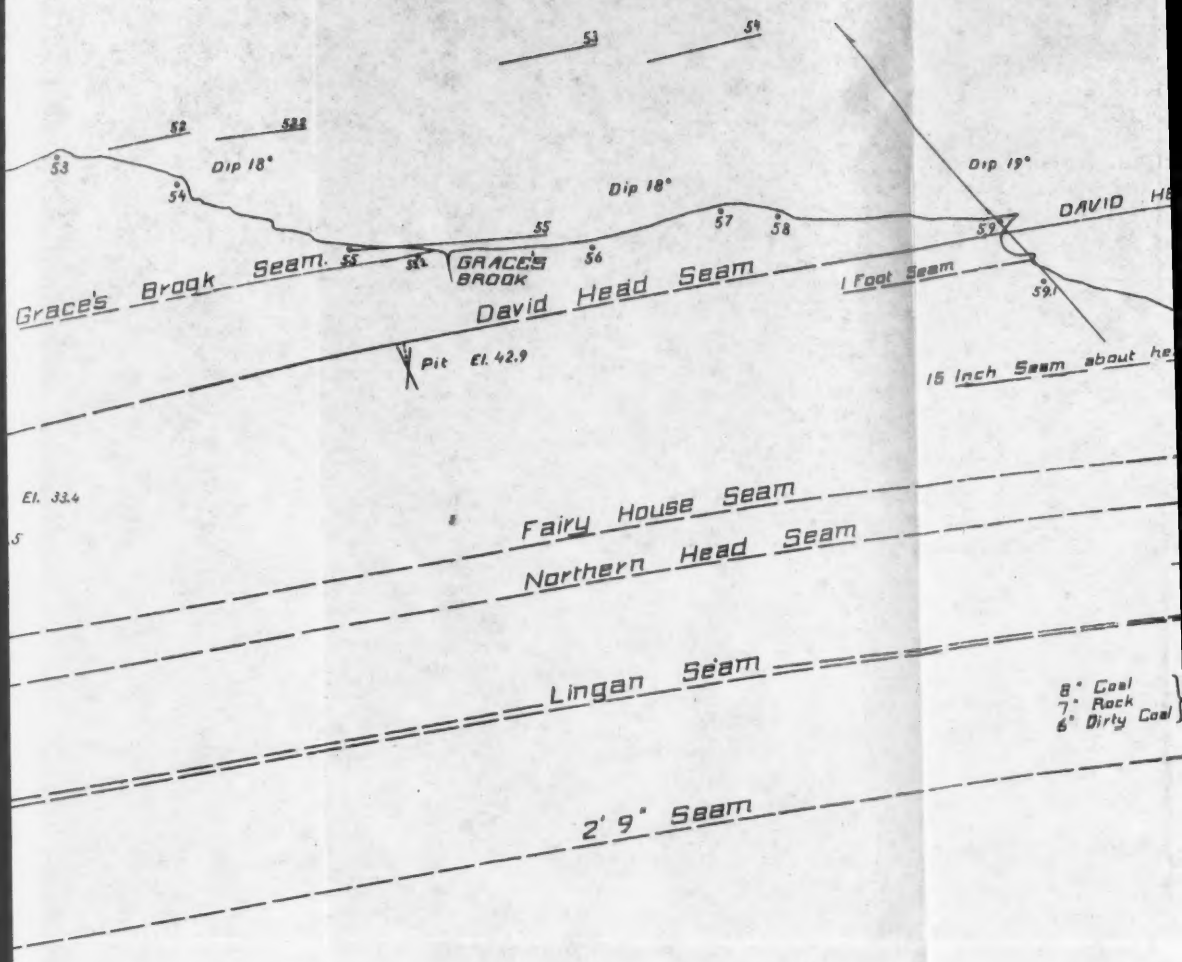
" COAL a

SANDSTON

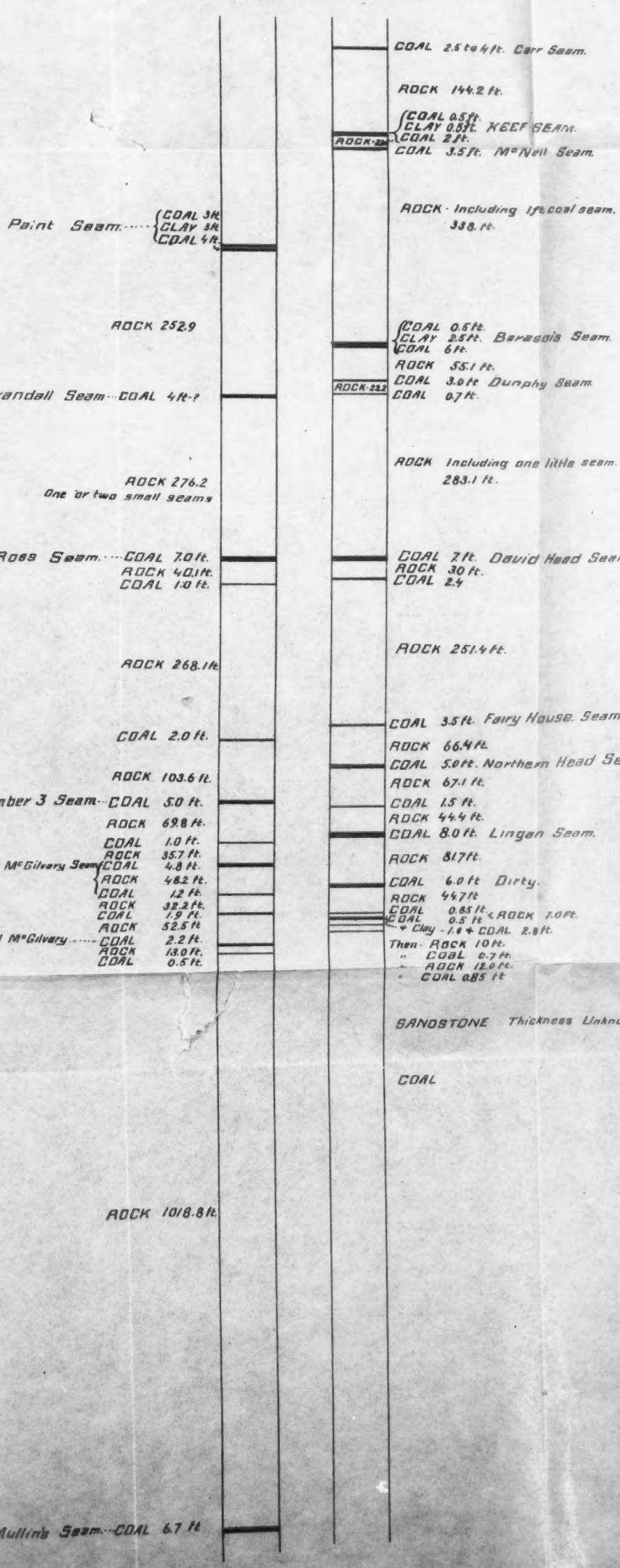
COAL

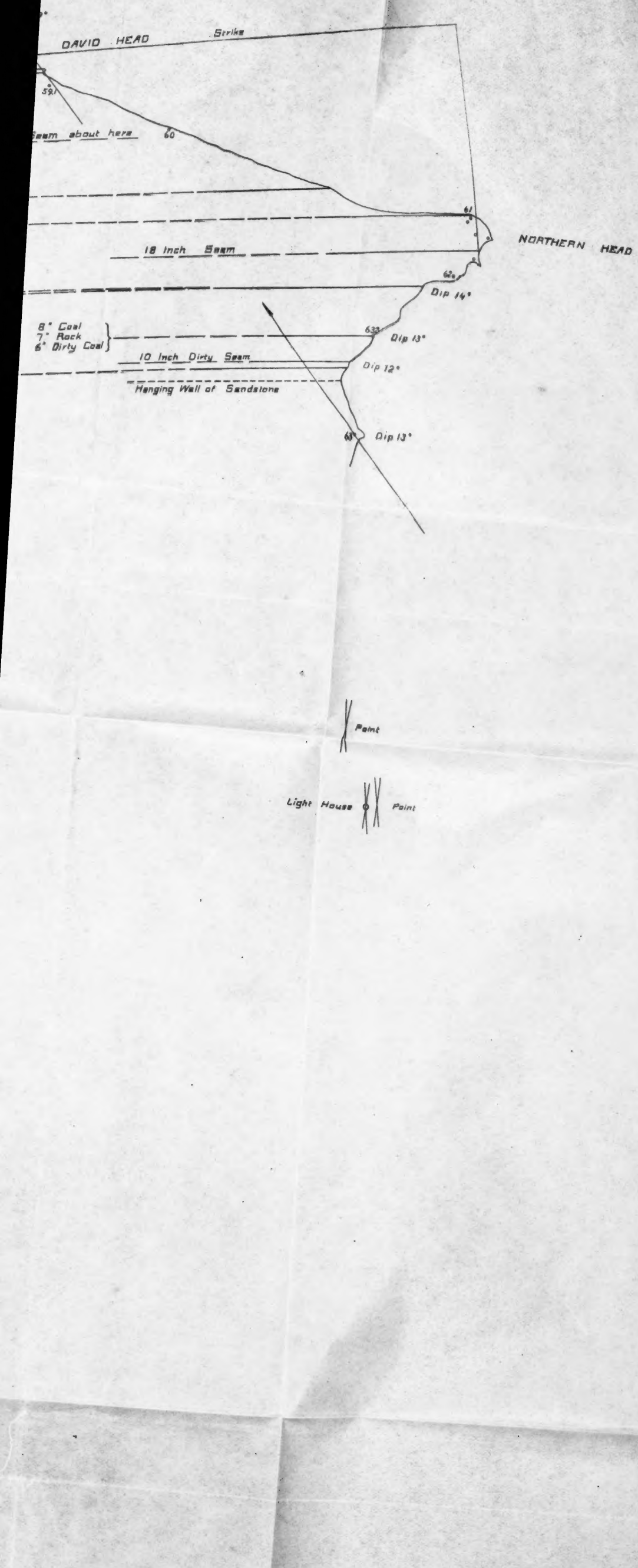
ROCK 1018.8 ft.

Mullin's Seam--COAL 6.7 ft



Victoria Section & Lingan Section.




DAVID HEAD
Strike
Seam about here
60
61
NORTHERN HEAD
18 Inch Seam
62½
Dip 14°
8" Coal
7" Rock
6" Dirty Coal
63½
Dip 13°
10 Inch Dirty Seam
Dip 12°
Hanging Wall of Sandstone
65
Dip 13°
Point
Light House
Point

out-of-door rambles, cannot fail to stimulate the mind of the most indifferent. When, as usually is the case, the visiting club is composed of young men thoroughly interested in all that may touch upon the many phases of historical architecture, the results obtained are not only highly satisfactory, but often of great historic interest.

The true student of architecture is not content with a simple glance or slight inspection, but, with pencil, measure, and book in hand, jots down details, notes, and general dimensions, that in later days the impression produced by the building visited may not be the only remembrance which he possesses. Often, also, these notes and rough sketches are rearranged or redrawn, and through the medium of either book or magazine are made still more valuable, since they then interest a large number of people.

In America we are handicapped in such work by the absence of good examples of the architecture of past generations. The grand cathedrals and the smaller but not less interesting churches and houses of mediæval times are here entirely lacking.

America, however, in its so-called "Colonial Architecture" possesses a class of buildings distinctly its own, which is not uninteresting or lacking in vitality. In the variations existing in the buildings erected in this country during the seventeenth, eighteenth, and early part of the nineteenth centuries we have an excellent opportunity for study. The simple and compact colonial house of the New England seaport town is not only quite different in character from the generous spaces and imposing façades of the Southern mansion of the same period, but many changes can also be found in the buildings of even the quietest of the older New England villages. These peculiarities in the general scheme, in the use of material, and in the arrangement of detail can only be appreciated by actual observation and intimate study of the architecture of these localities.

Taking into consideration, therefore, the historical value of these American buildings, the good results to be derived from serious inspection of existing structures, and, above all, the great beauty and delicacy of much of the colonial detail, the study of this style seems to be peculiarly fitted to supplement the classic course pursued by the students of the Architectural Department of the Institute.

During the spring of 1894 an opportunity was afforded for such study. On May 31 our party of sixteen left Boston for a three weeks' study of the old buildings of Salem, Newburyport, and Portsmouth.

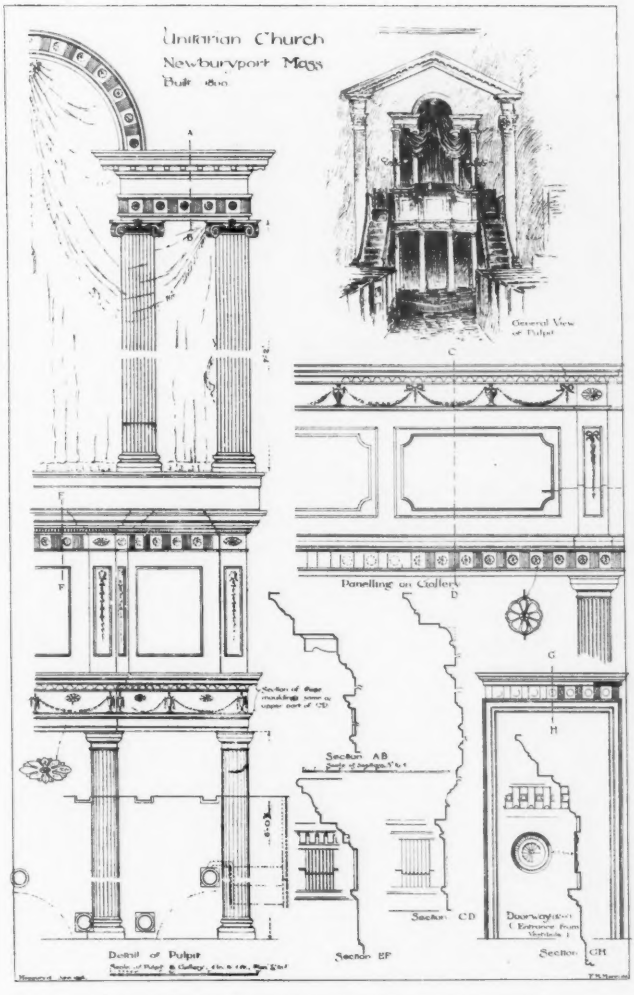
Thanks to the careful attentions of the officers of the Essex Institute, guides and carriages were quickly provided for a ride about town, and the afternoon passed only too rapidly while we were visiting the houses of the merchant princes of the past century. This general view, including the counting-rooms of Derby Street, the colonial houses of Essex, Franklin, and Chestnut Streets, many localities remembered for the distressing scenes of the witchcraft trials, and several places connected with the life of Hawthorne, gave us an excellent idea of the large number of interesting historical buildings which Salem still possesses.

Our first day away from Boston fittingly closed with the reception courteously given us by the Essex Institute. During this evening our architectural studies were very pleasantly encouraged by the good wishes of interested friends, and we had opportunities for meeting many of the people who during the next week so kindly opened their houses to us. Next morning, after listening to a talk on Hawthorne by Mr. Cousins, and looking over his large collection of Salem photographs, we visited the Nichols house (1798), the Whipple house, Hamilton Hall (1805), South Church (1804), Hodges house (1761), Washington Hall, and the Market and Town House (1790). Then began the assignment of buildings to be sketched and measured.

During the following two weeks spent in these three old seaport towns, we obtained a great quantity of measured drawings, full size details, sketches and photographs, visiting and in part measuring over thirty buildings in Salem alone. Nevertheless the excellent colonial architecture in these towns was by no means completely recorded, and after such a fair beginning the completion of this work is much to be desired.

Even in the short time which has elapsed since our visit, part of our work has proved to be of special historical interest, as one of the old buildings measured, the Timothy Orne house, Essex Street, Salem, erected in 1761, through the growth of the city has been so altered and changed for business purposes that nothing is now left of the excellent interior woodwork, which had remained in place for one hundred and thirty years.

Our longest stop was in Salem, but the few days spent at Newburyport and Portsmouth afforded an opportunity for a comparative view, at least, of the colonial architecture of these old towns. Both Newburyport and Portsmouth offer many excellent examples of brick



DETAILS FROM UNITARIAN CHURCH, NEWBURYPORT.
REDUCED FROM A SHEET 14″ x 21″.

Colonial Doorway,
Derby Street, Salem.

and wood residences dating from the last part of the eighteenth century. Several measured details and sketches were made of these houses, and a few water colors of the picturesque views along the water fronts, but the most serious work of the class was accomplished in the hospitable city of Salem.

The third week was spent at Boston in attempting to translate the mass of sketches and rough drawings made on the excursion, and in making careful scale drawings combining the most attractive fragments. Another year it is to be hoped that opportunity will be afforded for making the final drawings in the vicinity of the buildings measured.

As will be seen from the accompanying details from the Unitarian Church at Newburyport, parts of these finished drawings are made on a large scale in order to give the peculiarities of the moldings as well as the general proportions of the objects measured. To illustrate the attractive qualities of much of this old work a photograph, made by a member of the class from one of the old doorways of Salem, has also been inserted.

On Wednesday and Saturday afternoons our architectural studies were turned in new directions, since, although naval architecture was not included in the prospectus of the course, the vessels lying in the harbors of these old New England towns were then examined with the greatest interest. The long sails taken on these afternoons afforded keen enjoyment to all, the Western men of the party being particularly fascinated by the deep sea motion, the fresh Atlantic breezes, and the salty stories of our Yankee skippers.

SUMMER FIELDWORK IN MINERALOGY AND GEOLOGY.

The party for summer fieldwork in mineralogy and geology, under the charge of Professor W. O. Crosby, spent a fortnight last July in visiting the mines and mineral localities of Nova Scotia, and in studying the geological formations of that province. Landing at Yarmouth, and proceeding thence by rail to Wolfville, Windsor, and Halifax, particular attention was given, in passing, to the problems presented by the Annapolis Valley and the long line of the North Mountain which separates it from the Bay of Fundy. We saw very clearly that the valley is due to the relatively rapid erosion of the soft Triassic sandstone forming its floor, and that North Mountain is the outcropping edge

of a great sheet of trap interstratified with the sandstone, its level crest-line being best explained by regarding it as a remnant of an elevated peneplain. The continuation of this peneplain was found in the South Mountain on the other side of the valley.

At Windsor we made as careful a study as the time would permit of the highly fossiliferous carboniferous strata along the Avon River. A valuable series of fossils was obtained here, and from the similar limestones near Truro, for use in the Geological Laboratory of the Institute. Many of these are singularly well preserved, even the most delicate parts being almost as perfect as in recent specimens. In the extensive and interesting gypsum quarries at Wentworth, near Windsor, we noted especially that the gypsum is merely a surface alteration of the underlying anhydrite, and that the alteration takes place in this way: Passing upward from the unaltered anhydrite, minute veinlets of gypsum first appear in it; these become more numerous, and widen and coalesce more and more, until the anhydrite is reduced to small isolated remnants which finally disappear, and the alteration is complete. The gypsum quarries also afford admirable examples of chemical erosion in consequence of the ready solubility of the gypsum.

At Halifax we improved to the utmost the exceptionally good opportunity for the study of local metamorphism presented by the contact between the Cambrian slates and a great boss of granite. The exposures are so continuous and satisfactory that we were able as we approached the granite to trace every step in the metamorphism of an ordinary clay slate into a highly crystalline mica schist. This proved also to be a very favorable locality for the study of glacial phenomena. The glacial striæ and furrows are very distinct and perfect over the broad outcrops of metamorphic slate, and on the granitic area the perched and poised glacial erratics are a striking feature, the most notable of these being a rocking stone some twenty feet in diameter.

The gold mines at Montague and Waverly were visited from Halifax, and both the geology and mineralogy of the auriferous veins received due attention. The conclusion was reached that the very remarkable contorted vein at Waverly, affording the so-called "barrel" quartz, is an important link in the evidence that the auriferous quartz veins of this region are exogenous in origin, and were not formed in preëxisting open fissures.

At the Acadia Iron Mines in Londonderry we had an opportunity

for additional and very important paleontological work in the Subcarboniferous limestone, and obtained a good series of iron ores from this and other sections of the province. The Acadia mines afford an unusual variety of ores, but the chief ore, and the one giving character to the deposits, is the coarsely crystalline ankerite, a triple and variable carbonate of calcium, magnesium, and iron. The geological history of this great deposit of iron ore, which follows the base of the Cobequid Range for ten miles, we found to be, in outline, as follows: Contemporaneously with the deposition of the mud and sand which now form the inclosing slate and quartzite were deposited the carbonates of iron, lime, and magnesia, which subsequently formed the ankerite. Then followed the disturbance and tilting of the strata and the eruption of great masses of diorite and granite, by which the sedimentary rocks and especially the iron ores were metamorphosed, the ankerite, as it was recrystallized, being deposited in all the cracks and fissures of the inclosing strata. The small proportion of limonite originally mixed with the earthy carbonate was changed to specular hematite and magnetite. The deposit then remained essentially unchanged until erosion brought it within the reach of meteoric influences. The ferrous carbonate of the ankerite is now undergoing oxidation to limonite, and the hollow character of the limonite balls is due to the removal in solution of the associated calcium and magnesium carbonates.

A week was spent on the Parrsboro shore, where the Triassic trap sheets are so magnificently exposed, with their rich stores of minerals, and the conditions are so favorable for studying the relations of the Triassic beds to the great Carboniferous series. Valuable collections were made at Partridge Island, Wasson's Bluff, Amethyst Cove, Cape d'Or, etc., and many instructive illustrations of previous work in dynamic and structural geology noted.

The fieldwork closed with a visit to the celebrated section of the Carboniferous strata on the South Joggins shore. This is easily one of the most important geological sections in the world, and classic ground for the student of historical geology. We have here in one continuous section nearly three miles in thickness of strata embracing no fewer than seventy seams of coal, varying from a fraction of an inch to four feet in thickness, each seam having a floor of fire-clay and a roof of carbonaceous shales. Of special interest are the trunks of sigillaria and calamites standing perpendicular to the stratification

since they prove rapid deposition of the inclosing strata. Every layer of fire clay is a fossil soil, hence an ancient land surface. Every seam of coal is the compressed and carbonized vegetation that grew on that soil where the surface was of a marshy character. When a subsidence permitted the waves to wash mud over the marsh the formation of pure coal ceased, and there were formed instead the carbonaceous (coaly) shales covering the coal. And when the subsidence was sufficiently rapid the larger trees were buried to a depth of ten to twenty feet in mud and sand before they had time to decay and fall. This sequence of events was repeated over and over again during the formation of the Joggins strata. The extensive grindstone quarries and works at Lower Cove and the Joggins Coal Mine, 2,700 feet deep, also afforded us instructive and interesting experiences.

SUMMER INSTRUCTION IN THE CLASS ROOMS AND LABORATORIES OF THE INSTITUTE.

During a portion of the past summer vacation instruction was for the first time given in the lecture rooms and laboratories of the Institute by members of its instructing force. These summer courses partook of the character of private instruction, sanctioned by the Faculty, and were originated in the belief that students of the Institute having arrears at the close of the year would avail themselves of an opportunity to make up such deficiencies by summer work, in order that they might enter succeeding years unhampered by this necessity for extra labor. Students with clear records would be enabled, through this instruction, to acquaint themselves with subjects which, though not included in the schedules of their respective courses, might prove to be valuable helps in professional work. Still others, it was thought, might gain additional experience in professional work itself beyond that possible in the prescribed courses of the Institute.

During June and July, 1894, courses of six weeks' duration each were offered as follows: French and German, by Professors van Daell and Dippold; Analytical Chemistry, by Professor Talbot; General Chemistry, by Professor Bardwell; Organic Chemistry, by Dr. Evans; Physics, by Mr. Wendell; Analytic Geometry and Integral Calculus, by Mr. George; Descriptive Geometry, by Mr. C. M. Faunce.

The students attending these courses represented every class for

whom the courses were designed, and the hearty way in which the work was carried on seemed to indicate a gratifying appreciation of the opportunities offered. The announcement of the list of subjects in which instruction would be given was necessarily delayed until the closing days of the Institute year, to which may be attributed the fact that the attendance last summer was comparatively small. The introduction of these courses at this time was wholly tentative, but the results of the experiment seem to point to a successful future for summer instruction.

THE INSTITUTE AND THE STUDY OF THE PREVENTION OF LOSS BY FIRE.[1]

BOSTON MANUFACTURERS' MUTUAL FIRE INSURANCE CO.
March, 1895.

PRESIDENT FRANCIS A. WALKER.

Dear Sir: In the conduct of the work of developing the science of preventing loss by fire, establishing the principles of mill construction, and perfecting appliances for putting out fires, the work of the professors, graduates, and students of the Massachusetts Institute of Technology has been of paramount influence. The subjects which it has been necessary to investigate and by scientific methods to bring into common practice are many.

1. *Lubrication.* The introduction of the mineral or paraffine oils has made a complete revolution in the matter of lubrication, doing away, so far as they are used, with the danger of spontaneous combustion, but subjecting factories to other hazards. The work of developing this subject was intrusted to Professor John M. Ordway, and he was assisted by Mr. C. J. H. Woodbury, a student of the Institute and an employee of this company. Mr. Charles N. Waite, a graduate of the Institute, also did much valuable work in establishing the science of lubrication. One result of this investigation was the invention of the only existing machine for determining the coefficient of friction. The final result was a complete revolution in the distillation of oil, and an annual saving to the members of this company only, more than equal to, in fact many times in excess annually of the sum which you now ask from the State in order to maintain your present position. The influence of this investigation has spread throughout the community, changing all the conditions and diminishing the hazard of fire.

2. Other oils, animal and vegetable, which are made use of on wool and in other ways, *the science of oil* if it may be so called, was investigated. Apparatus for getting up rapid oxidation, commonly

[1] This statement was prepared for presentation to the Finance Committee of the House of Representatives by Edward Atkinson, Esq., President of the Boston Manufacturers' Mutual Insurance Co. As no public hearing was given by the committee it was not used for this purpose.

called spontaneous combustion, was invented. The subject of the treatment of wool by naphtha for cleansing purposes, which is now becoming a very important factor, was thoroughly worked up by Mrs. Ellen H. Richards, and included in a report under date of May 5, 1879. Tests for adulteration were established, and from that time to the present scarcely a month has passed without my being called upon to send examples of oil to Mrs. Richards to be passed upon on questions of safety, purity, and the like.

3. *Automatic sprinklers.* In 1880 it became apparent to me that some new safeguard must be found to meet the increasing danger of high speed, rapidly oxidizing dye stuffs and other materials, and increasing floor areas. The automatic sprinkler had then been invented. It became necessary to study the nature of the fusible solder or alloy used therein, to determine its durability, and to decide in advance what would be the effect of water sealed up for many years upon metals, in the expectation of its being released by the heat of a fire in thirty to sixty seconds. The investigation was complete. It was conducted in the metallurgical department, and exhaustive experiments were made by Mr. Woodbury. Subsequently the whole matter has been in the charge of Mr. John R. Freeman, a graduate of the Institute. There is no appliance in existence which has saved so much property from destruction, relatively to its cost, as this appliance.

4. The friction of water in iron pipes, in leather and fabric hose, has been conducted mainly under the charge of Mr. John R. Freeman, and from these experiments the hydraulics of fire protection have been established upon a scientific basis. Standards of hose and of play pipes have been established under the name of the "Underwriter Hose and Play Pipe." Smooth weaving has been substituted for rough weaving in fabric hose, greatly diminishing friction, and therefore lessening the danger of bursting the hose. The friction of water in iron pipes has been reduced to rules, which have enabled me to put before every member in simple terms the information by which a lay-out of a fire service can be readily made. The construction of the steam fire pump has also been greatly improved by Mr. Freeman, and the "Underwriter Pump" made on the specifications established by him is now the standard fire pump.

5. Electricity has called for very serious attention, having been introduced in the factories under my charge before any general development had occurred. With the aid of Professor Cross and others,

graduates of the Institute, rules were established for installing electric plants, which have become the common rules throughout this country. They have been subject to variation with the development of the science, but no material change has been made. All the electric companies of repute have coöperated with us, and our present inspector of electric plants is Mr. E. V. French, a graduate of the Institute. The advice of Professor William L. Puffer, of the Institute, has been of great value to us in keeping pace with the rapid changes in the electric arts and in guarding against the fire hazard therefrom. To-day we rely upon the electrical laboratories of the Institute for our most important electrical tests, and upon Professor Puffer as our consulting electrical expert.

6. The system of slow burning or mill construction has been perfected. It is now becoming the common practice all over the country in works and warehouses, even those that never come under the supervision of the Factory Mutual Insurance Companies. In the development of this subject the tests of timber, made by Professor Lanza with the apparatus of the Institute, have served a most valuable purpose.

7. Many substances which are used for the purpose of retarding fire — compounds, paints, etc. — have been tested at the Institute. The rubbish has been rejected and the useful kinds have been established.

8. The whole subject of the covering of steam pipes and boilers was treated exhaustively by Professor John M. Ordway, and from the results of those tests new inventions have ensued to the great benefit of all steam users.

9. The subject of glazing is under treatment. It is probable that hereafter factories and workshops will be glazed mainly with fine ribbed glass, diffusing the light and stopping the glare. The photometric measurements and the photographic images which have enabled me to develop this subject were made by Mr. Charles W. Hinman, a graduate of the Institute. Many other minor subjects have been dealt with, and there yet remains a great deal of work to be done.

10. The conductivity of glass with respect to heat is under consideration.

11. A joint undertaking to determine the science of bricks, mortars, and cements is under way, with the coöperation of Professor Shaler, of the Lawrence Scientific School.

12. The subject of smoke prevention is pressing for solution.

13. The protection of iron and steel from heat and from rust, in buildings framed of these metals, is a subject of paramount importance.

It is possible that all this work could have been done had there not been a Massachusetts Institute of Technology, but it would have taken a very much longer period of time, with less assurance of true results.

There are now in the service of the Factory Mutual Insurance Companies the following graduates and students of the Institute:

Mr. Joseph P. Gray, vice-president of this company.

Mr. John R. Freeman, chief of the Bureau of Inspections.

Messrs. Waldo E. Buck, Loammi F. Baldwin, Frank L. Pierce, B. G. Buttolph, Macy S. Pope, Harry B. Burley, and E. V. French, inspectors and assistants.

Mr. L. H. Kunhardt, head draftsman.

Messrs. S. N. Braman, J. G. Morse, A. L. Kendall, F. M. Heermann, E. D. Pingree, and J. H. Howland, draftsmen.

The outside experts to whom we frequently refer members for professional assistance are Messrs. Charles T. Main, C. W. Hinman, and Harvey S. Chase, graduates of the Institute.

For myself I can only say that, never having enjoyed the training either of the university or of the technical school, I could never have developed even the conception of the science of preventing fires except for the support, aid, and instruction which I constantly derived during my long intercourse with the late William B. Rogers, whom it was my privilege to support for so many years in the early history of the school.

If it will be of any service for me to appear before the Finance Committee on the application of the Institute of Technology for a little more State aid, I think it may be of great interest to them for me to develop these matters more fully in detail, and by reference to our various accounts to give them some idea of the magnitude of this work, which counts for a saving to the manufacturing community of this section in millions of dollars.

Respectfully submitted,

EDWARD ATKINSON.

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DEFOE. History of the plague in London. 1894.
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Marmion. 1893.
Woodstock. 1894.
SHAKSPEARE. Merchant of Venice. 1893.
Midsummer Night's dream. 1894.
Twelfth Night. 1892.
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Abbot. 1893.
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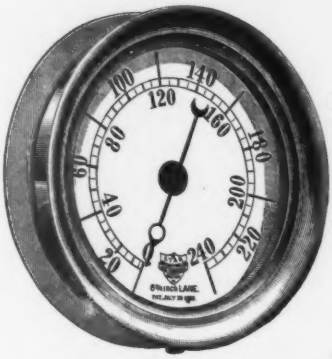

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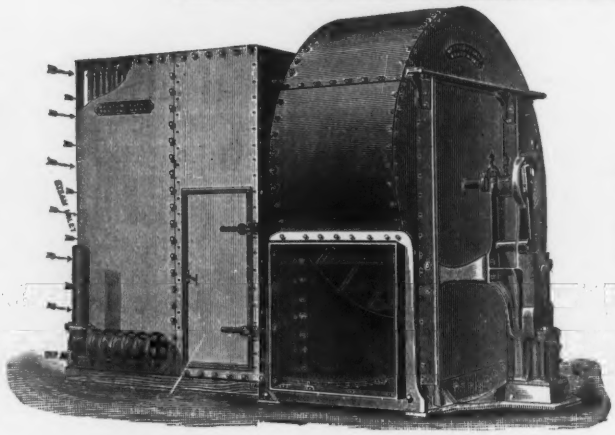

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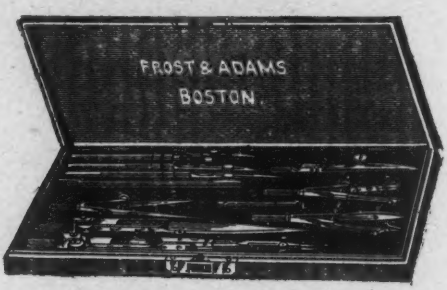

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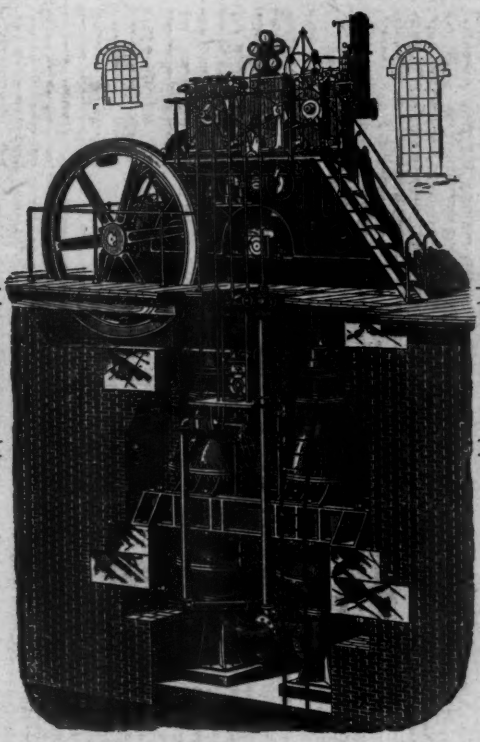

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